



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b>  <b>A23L 1/308</b>	<b>A2</b>	<b>(11) International Publication Number:</b> <b>WO 98/52428</b>  <b>(43) International Publication Date:</b> 26 November 1998 (26.11.98)
<b>(21) International Application Number:</b> PCT/US98/10316  <b>(22) International Filing Date:</b> 20 May 1998 (20.05.98)  <b>(30) Priority Data:</b> 60/047,176                      20 May 1997 (20.05.97)                      US  <b>(71) Applicant (for all designated States except US):</b> THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VOLKER, Alan, David [US/US]; 8337 Waradmiral Drive, North Bend, OH 45052 (US). HOWIE, John, Keeney [US/US]; 5958 Olive Branch Road, Oregonia, OH 45054 (US).  <b>(74) Agents:</b> REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> A FLOWABLE COMPOSITION AND A PROCESS FOR MAKING THE FLOWABLE COMPOSITION  <b>(57) Abstract</b>  A flowable nondigestible oil composition having a Consistency in a temperature range of 20 °C to 40 °C of less than about 600 P.sec <sup>(n-1)</sup> , preferably less than about 400 p.sec <sup>(n-1)</sup> . The flowable nondigestible oil contains a liquid component having a complete melt point less than 37 °C. and a solid component having a complete melt point of at least about 37 °C. At least one of the solid component and the liquid component includes a material selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof. A method for making the composition is also disclosed.		

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## A FLOWABLE COMPOSITION AND A PROCESS FOR MAKING THE FLOWABLE COMPOSITION

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### FIELD OF THE INVENTION

This invention relates to a flowable nondigestible oil composition containing a solid nondigestible oil component, which can flow at ordinary and ambient storage temperatures, and to a process for making the flowable nondigestible oil.

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### BACKGROUND ART

Numerous patents have been directed to providing materials which have the physical and gustatory characteristics of triglyceride fats, but which are absorbed to a low extent or not at all by the body. These materials are referred to variously as noncaloric fats, pseudofats, nondigestible fats and fat substitutes. Patents pertaining to such materials include U.S. Pat. Nos. 4,582,927, Fulcher, issued April 15, 1986, (fatty esters of malonic acid); 4,582,715, Volpenhein, issued April 15, 1986, (alpha acetylated triglycerides); and 3,579,548, Whyte, issued May 18, 1981, (triglycerides of alpha-branched chain carboxylic acids).

One particular type of compound which has achieved considerable attention as a nondigestible fat is sucrose polyester (i.e., sucrose in which at least four of the eight hydroxyl groups are esterified with a fatty acid). U.S. Pats. 3,600,186, Mattson, issued Aug. 17, 1971; 4,368,213, Hollenbach et al. issued January 11, 1983; and 4,461,782, Robbins et al. issued July 24, 1984 describe the use of this material as a nondigestible fat in a variety of food compositions.

A problem associated with use of liquid nondigestible oils, i.e., those having a melting point below body temperature (about 37°C), is an undesired passive oil loss effect, which is manifested in leakage of the liquid nondigested fat through the gastrointestinal tract's anal sphincter. Regular ingestion of moderate to high levels of completely liquid forms of these polyol polyesters can produce this passive oil loss. U.S. Pat. No. 4,005,195, Jandacek, issued Jan. 25, 1977, discloses the combining of higher melting fatty materials such as solid triglycerides and solid sucrose polyesters with the liquid sucrose polyesters in order to control oil loss.

U.S. Pat. 4,797,300 (Jandacek et al.), issued January 10, 1989 discloses the use of certain solid sucrose polyesters which have high oil binding capacity for liquid sucrose polyesters (SPE) and liquid triglycerides, when used at levels of about 10% to 25% in said oils. It is disclosed that because of their high oil binding capacity, these solid sucrose polyesters have outstanding utility as agents to prevent passive oil loss of liquid nondigestible sucrose polyesters, and they are also useful as non-caloric hardstocks to use with liquid digestible or nondigestible oils in the preparation of semi-solid fat products such as shortenings and margarines. The oil binding agents of the Jandacek et al. '300 patent are solid sucrose polyesters wherein the ester groups consist essentially of a mixture of short chain saturated fatty acid ester radicals ( $C_2$ - $C_{10}$ ) and long chain saturated fatty acid radicals ( $C_{20}$ - $C_{24}$ ) in a molar ratio of short chain to long chain of from about 3:5 to about 5:3, and wherein the degree of esterification is from about 7 to about 8. Jandacek et al. also disclose plastic shortening and other food compositions containing 10-25% of the solid SPE.

U.S. Patent 4,005,195 (Jandacek), issued January 25, 1977 describes a means of preventing the undesirable oil loss effect through the addition of the polyesters as oil-loss control agents. The oil-loss control agents include solid fatty acids (melting point  $37^{\circ}\text{C}$  or higher) and their triglyceride sources, and solid polyol fatty acid polyesters. Specifically  $C_{10}$ - $C_{22}$  saturated fatty acid polyesters are said to be useful at levels of at least 10%, preferably at least 20%.

U.S. Patent 5,306,514 (Letton et al.), issued April 26, 1994, discloses edible oil compositions containing a) a liquid nondigestible oil having a complete melting point below about  $37^{\circ}\text{C}$ , and b) a solid polyol fatty acid polyester having a complete melting point above about  $37^{\circ}\text{C}$ , wherein the weight ratio of b) to a) is from about 1:99 to about 9:91. The solid polyol fatty acid polyester consists of (i) a polyol having at least about 4 hydroxyl groups, wherein at least about 4 of the hydroxyl groups of the polyol are esterified, and (ii) ester groups comprised of (a) fatty acid radicals selected from the group consisting of  $C_{12}$  or higher unsaturated fatty acid radicals,  $C_2$ - $C_{12}$  saturated fatty acid radicals, or mixtures thereof, and (b)  $C_{20}$  or higher saturated fatty acid radicals, at a molar ratio of (a):(b) being from about 1:15 to about 1:1. In the solid polyol polyester at least 15% by weight of the fatty acid radicals  $C_{20}$  or higher saturated fatty acid radicals. Further, the slope of the SFC profile of the mixture of a) and b) between  $37^{\circ}\text{C}$  and  $21.1^{\circ}\text{C}$  is between 0 and about -.75.

U.S. Patent 5,306,515 (Letton et al.), issued April 26, 1994, discloses pourable compositions containing a solid polyol fatty acid polyester, having a complete melting point above about  $37^{\circ}\text{C}$ , a liquid nondigestible oil having a complete melting point below about  $37^{\circ}\text{C}$ , less than about 90% by weight of a digestible oil having less than 5% solids at  $21^{\circ}\text{C}$ ; and less than 10% hardstock; wherein the ratio of (A) to (B) is from about 1:99 to about 9:91 and wherein the pourable composition has a yield point of not more than about 100 dynes/cm<sup>2</sup>.

The solid polyol fatty acid polyester consists of (i) a polyol having at least about 4 hydroxyl groups, wherein at least about 4 of the hydroxyl groups of the polyol are esterified, and (ii) ester groups comprised of (a) fatty acid radicals selected from the group consisting of C<sub>12</sub> or higher unsaturated fatty acid radicals, C<sub>2</sub>-C<sub>12</sub> saturated fatty acid radicals or mixtures thereof, and (b) C<sub>20</sub> or higher saturated fatty acid radicals at a molar ratio of (a):(b) being from about 1:15 to about 2:1. In the solid polyol polyester at least 15% by weight of the fatty acid radicals are C<sub>20</sub> or higher saturated fatty acid radicals. Further, the slope of the SFC profile of the mixture of (A) and (B) between 37°C and 21.1°C is between 0 and about -.75, and the combined level of (A) and (B) in said composition is at least 10% by weight.

10 Examples include compositions containing 65 wt. % liquid digestible triglyceride oil.

Additionally, the following patent documents provide description related to esterified propoxylated glycerins, esterified linked alkoxylated glycerins, and/or esterified epoxide extended polyols: U.S. Patents 4,861,613 to Pollard; 4,983,329 to Cooper; 5,175,323 to Cooper; 5,273,772 to Cooper; 5,304,665 to Cooper; 5,399,728 to Cooper; 5,512,213 to Cooper; 5,603,978 to White; 5,641,534 to White; EPO Patent Documents 325,010 published July 26, 1989 in the name of White et al.; 667,105 published August 16, 1995 in the name of Ziegert et al.; PCT Publication WO 97/222260; U.S. Patents 5,273,772 to Cooper; 5,362,894 to Handweker; 5,374,446 to Ferenz; 5,427,815 to Ferenz; 5,516,544 to Sekula;

20 EPO Patent Document 571,219 published November 24, 1993 in the name of Masten.

### SUMMARY OF THE INVENTION

5 It is an object of the present invention to provide a flowable nondigestible oil composition containing a solid component at ambient temperature, which flowable oil composition is flowable at ordinary and ambient temperatures, and which flowable oil composition can subsequently be used as an edible nondigestible or partially digestible oil providing good passive oil loss control and good organoleptic properties to foods prepared with them.

10 According to one aspect of the present invention, a flowable nondigestible composition, such as a flowable nondigestible oil composition, is provided. The flowable composition comprises a liquid component having a complete melt point less than 37°C and a solid component having a complete melt point of at least about 37°C, wherein the solid component is in the form of crystallized particles. One or both of the liquid and solid  
15 components comprises a material selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof.

In one embodiment, the solid component comprises a material selected from esterified  
20 linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof; and the liquid component comprises a liquid non-alkoxyated polyol fatty acid polyester such as a liquid sucrose polyester.

In another embodiment, the solid component comprises a solid non-alkoxyated polyol fatty acid polyester, such as a sucrose polyester, and the liquid component comprises a  
25 material selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof.

In yet another embodiment, solid component comprises a material selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines;  
30 esterified epoxide-extended polyols; and mixtures thereof; and the liquid component comprises a material selected from liquid esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof.

The flowable composition has a Consistency (K) within the temperature range of 20-40 °C of less than about 600 P.sec<sup>(n-1)</sup>, where K is determined from a power law model fit of the apparent viscosity versus shear rate data (see Analytical Method Section), and n is the shear index (dimensionless). In one embodiment, the composition can have a Consistency of  
5 less than about 400, more particularly less than about 200, and still more particularly less than about 100 P.sec<sup>(n-1)</sup> in a temperature range of 20-40 degrees Centigrade.

The flowable composition can contain the solid component in the form of small crystal particles, typically having a largest dimension of less than about 30 microns, preferably less than about 10 microns, more preferably between 1 and 30 microns, even more  
10 preferably between 1 and 10 microns, and most preferably of about 2 to about 5 microns.

The present invention also provides a process for making a flowable nondigestible oil composition comprising a liquid component having a complete melt point less than 37°C, and a solid component having a complete melt point of at least about 37°C. The process comprises the steps of:

- 15 a) providing a mixture comprising the liquid component and the solid component, wherein at least one of the liquid component and the solid component comprises a material selected from esterified linked alkoxylated polyols, such as esterified linked alkoxylated glycerines; esterified epoxide-extended polyols; and mixtures thereof ;
- b) melting the mixture of the liquid component and the solid component;
- 20 c) crystallizing at least a substantial portion of the solid component; and
- d) shearing the mixture of the liquid component and the solid component during the step of crystallizing, thereby forming at least a substantial portion of the solid component into crystallized particles.

25 According to one embodiment, the process comprises the steps of melting completely the mixture containing the solid component, rapidly cooling the melted mixture to a crystallization temperature, thereby rapidly crystallizing at least a substantial portion of the solid component, and shearing the mixture during the step of crystallizing to form the flowable nondigestible oil composition. Optionally, following the crystallizing and shearing  
30 steps, the process can include one or both of the following steps: 1) the step of tempering the crystallized nondigestible oil composition for a time sufficient to substantially completely crystallize all of the solid component, and/or 2) the step of adding a stabilizing amount of a diluent liquid, typically a liquid polyol fatty acid polyester, to the crystallized nondigestible oil composition, or both steps.

These compositions are capable of being stored in a flowable state at ambient and ordinary storage temperatures. Storage at ambient and ordinary temperature avoids exposure of the composition to high temperatures (generally greater than 50 °C) usually associated with storage and handling of the nondigestible oil composition in a molten form. Making and storing the nondigestible oil in a flowable form allows the nondigestible oil to be easily handled at ambient handling and storage temperatures, which minimizes the effect of heat and high temperature on the chemical stability of the polyol fatty acid polyester. This results in greater oxidative and flavor stability during extended storage of the nondigestible oil and of food products containing the nondigestible oil. This is particularly advantageous when the liquid component of the nondigestible oil is made from an unhardened (non-hydrogenated) source oil, such as unhardened cottonseed oil. In addition, the flowable nondigestible oil of the present invention can be utilized as a carrier for the application or incorporation of ingredients to foods products, such as flavorings, seasonings, and vitamins.

Without being limited by theory, it is believed that the use of esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof, provide the advantage that the flowable composition having such materials are less likely to be associated with gastro-intestinal symptoms than are flowable compositions which do not include such materials.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1a through 1c depict sucrose octaester monomer, dimer and trimer, respectively.

#### DEFINITIONS

As used herein the term "nondigestible " shall mean being absorbable to an extent of only 70% or less (especially 40% or less, more particularly 20% or less) by the human body through its digestive system.

As used herein, the term "flowable" refers to ability of a composition to be transported by gravity or by conventional mechanical or pneumatic pumping means from a storage vessel.

As used herein the term "ambient" shall mean a temperature which is less than the lowest onset crystallization temperature of a solid polyol fatty acid polyester in the nondigestible oil composition.

As used herein, the term "food" refers to any manner of viand for usage by man. "Food" may further include individual food components or mixtures thereof.

As used herein, the term "comprising" means various components can be conjointly employed in the fat compositions of the present invention. Accordingly, the term



"comprising" encompasses the more restrictive terms "consisting essentially of" and "consisting of".

All percentages and proportions herein are by weight unless otherwise specified.

#### DETAILED DESCRIPTION OF THE INVENTION

5 High temperatures and exposure to oxygen can result in thermal and oxidative decomposition of the nondigestible oil composition. It is preferred to avoid storage and handling of the nondigestible oil at the higher temperatures provided in heated railway cars and production tanks, which are needed to maintain the nondigestible oil in a molten state.

Consequently, there is a significant advantage to store and transport the nondigestible  
10 oil at lower, ambient temperatures, and in the absence of oxygen, to inhibit or reduce thermal and oxidative degradation of the nondigestible oil composition, to improve the quality of the nondigestible oil composition and the foods prepared therewith, and to require less expensive and less complicated transportation and storage requirements for the nondigestible oil composition. Generally, the ambient temperature at which the flowable nondigestible oil of  
15 the present invention would be stored is from about 5°C to about 50°C, and more preferably from about 20°C to about 40°C.

To commercially process the nondigestible oil economically and in large quantities, there is a need for a rapid process to make a flowable nondigestible oil composition which can be handled and stored at ambient temperature. Such a process would convert the  
20 nondigestible oil into a flowable nondigestible oil at ambient conditions in less than 2 hours, preferably in less than one hour, and more preferably in less than 30 minutes. For commercial reasons, the flowable nondigestible oil composition of the present invention should have good flow properties, such that the flowable nondigestible oil will drain sufficiently, preferably substantially completely, by the force of gravity from the inside of  
25 transportation vessels, such as railway cars, and manufacturing containers, such as tanks. Preferably, the flowable nondigestible oil composition of the present invention generally will not adhere in a mass to the side walls and other surfaces inside the railway cars or tanks. That is, the flowable nondigestible oil will typically drain such that only a relatively thin layer or film of the nondigestible oil will remain on the inside surfaces of a vessel or tank.  
30 Preferably, the flowable nondigestible oil is stable during extended storage; that is, it remains flowable and there is minimal and preferably no separation or settling of the solid crystals.

##### I. Composition of Flowable Nondigestible Oil

A flowable nondigestible oil composition comprising a solid component having a complete melting point of at least about 37°C and a liquid component having a complete  
35 melting point of less than about 37°C, can be prepared which is flowable at ambient storage

temperatures, and can, upon further processing including remelting completely the solid component, provide good passive oil loss control and organoleptic properties (i.e. good mouthfeel) to foods prepared therewith.

5 The flowable nondigestible oil composition of the present invention generally comprises about 50% to about 99%, more preferably about 80% to about 97%, and most preferably about 85% to about 95%, of the liquid component. In one embodiment, the solid component comprises a solid sucrose polyester, and the flowable nondigestible oil composition comprises about 1% to about 50%, more preferably about 3% to about 20%, and most preferably about 5% to 15%, of the solid sucrose polyester. In another  
10 embodiment, the solid component comprises a material selected from esterified linked alkoxyated polyols, esterified epoxide extended polyols, and mixtures thereof; and the flowable nondigestible oil composition comprises about 1% to about 50%, more preferably about 5% to about 30%, of the solid component.

The flowable nondigestible oil composition generally has a Consistency of less than  
15 600 P.sec(n-1) in a temperature range of from 20-40°C. The flowable nondigestible oil composition can have a Consistency of preferably less than about 400 P.sec(n-1), more particularly less than about 200 P.sec(n-1), and still more particularly less than about 100 P.sec(n-1), in a temperature range of 20-40°C.

The compositions according to the present invention are further characterized in  
20 having a relatively flat solids content profile across the temperature range of from typical room temperature to body temperature, i.e., from about 21.1°C (70°F) to about 37°C (98.6°F). The slope of the SFC profile is expressed as the change in percent solids per unit change in temperature, in °F. Typically the slope of the Solid Fat Content (SFC) profile between these temperatures is between 0 and -0.75. More particularly, the slope can be between 0 and  
25 -0.5, and still more particularly between 0 and -0.3.

Generally, where the solid component comprises C20 or higher saturated fatty acid radicals, the higher the weight percent of C20 or higher saturated fatty acid radicals in the solid polyol polyester, the flatter the SFC profile slope will be. For example, if the solid component comprises solid polyol polyester containing C20 or higher saturated fatty acid  
30 radicals, then at the 30% C20 or higher fatty acid level the slope can be between 0 and -0.5, and at 50% it will typically be between 0 and -0.3.

Determination of SFC values over a range of temperatures can be done by a method involving PNMR (Pulsed Nuclear Magnetic Resonance). Such method is well known to those skilled in the art (see J. Amer. Oil Chem. Soc., Vol. 55 (1978), pp. 328-31, and  
35 A.O.C.S. Official Method Cd. 16-81, Official Methods and Recommended Practices of The American Oil Chemists Society, 3rd. Ed., 1987; both incorporated herein by reference).

In one embodiment, the solid component comprises a material selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof; and the liquid component comprises a liquid non-alkoxyated polyol fatty acid polyester such as a liquid sucrose polyester.

5 In another embodiment, the solid component comprises a solid non-alkoxyated polyol fatty acid polyester, such as a sucrose polyester, and the liquid component comprises a material selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof.

10 In yet another embodiment, solid component comprises a material selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof; and the liquid component comprises a material selected from liquid esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof.  
15 thereof.

Suitable alkoxyated polyols include alkoxyated glycerol, alkoxyated polyglycerols, sorbitol alkoxyated glycerins, alkoxyated polysaccharides, and linked alkoxyated polyols such as linked alkoxyated glycerins. Polyols may be alkoxyated  
20 with C<sub>3</sub>-C<sub>6</sub> epoxides, such as propylene oxide, butylene oxide, isobutylene oxide, and pentene oxide, to produce epoxide-extended polyols having an epoxylation index minimum of at least about 2, preferably in the range of from about 2 to about 8, as described in U. S. Patent No. 4,816,613, incorporated herein by reference. Polyols may be also alkoxyated with an epoxide, preferably a C<sub>3</sub>-C<sub>10</sub> 1,2-alkylene oxide, in the  
25 presence of a ring-opening polymerization catalyst, as described in U. S. Patent Nos. 5,399,729 and 5,512,313, incorporated herein by reference.

Suitable alkoxyated polyols are also described in U. S. Patent Nos. 4,983,329; 5,175,323; 5,288,884; 5,298,637; 5,362,894; 5,387,429; 5,446,843; 5,589,217; 5,597,605; 5,603,978 and 5,641,534, all incorporated herein by reference. Suitable  
30 alkoxyated polyols include alkoxyated sugar alcohols, alkoxyated monosaccharides, alkoxyated disaccharides, alkoxyated polysaccharides, alkoxyated C<sub>2</sub> - C<sub>10</sub> aliphatic diols, and alkoxyated C<sub>3</sub> -C<sub>12</sub> aliphatic triols. Preferred alkoxyated C<sub>3</sub> -C<sub>12</sub> aliphatic triols are alkoxyated glycerols, more preferred are propoxylated glycerols, and particularly preferred are propoxylated glycerols having from about 3 to about 21 moles  
35 of propylene oxide per mole glycerol. Preferred alkoxyated polysaccharides are alkoxyated polysaccharides containing anhydromonosaccharide units, more preferred are

propoxylated polysaccharides containing anhydromonosaccharide units, as described in U. S. Patent No. 5,273,772, incorporated herein by reference. Suitable linked alkoxyated glycerins include those comprising polyether glycol linking segments, as described in U.S. Patent No. 5,374,446, incorporated herein by reference, and those comprising polycarboxylate linking segments, as described in U. S. Patent Nos. 5,427,815 and 5,516,544, incorporated herein by reference; more preferred are those described in U. S. Patent No. 5,516,544.

As used herein, the term "polyol fatty acid polyesters" is intended to include fatty acid esters of polyols, in which the hydroxyl groups are replaced with esters of fatty acids. Suitable fatty acid esters can be derived from either saturated or unsaturated fatty acids. Suitable preferred fatty acids include, for example, capric, lauric, palmitic, stearic, behenic, isomyristic, isomargaric, myristic, caprylic, and anteisoarachadic. Suitable preferred unsaturated fatty acids include, for example, maleic, linoleic, licanic, oleic, elaidic, linolenic, erythrogonic acids. In a preferred embodiment of the invention the fatty acid chains of the esterified polyols have from about two to about twenty-four carbon atoms. Polyol fatty acid polyesters obtained from naturally occurring oil such as soybean oil, cottonseed oil, palm kernel oil, palm oil, coconut oil, sunflower oil, safflower oil, rapeseed oil, high erucic acid rapeseed oil, canola oil, tallow oil, peanut oil and corn oil are preferred. The oils can be fully hydrogenated or partially hydrogenated oils.

Suitable polyol fatty acid polyesters are esterified linked alkoxyated glycerins, including those comprising polyether glycol linking segments, as described in U.S. Patent No. 5,374,446, incorporated herein by reference, and those comprising polycarboxylate linking segments, as described in U. S. Patent Nos. 5,427,815 and 5,516,544, incorporated herein by reference; more preferred are those described in U. S. Patent No. 5,516,544.

Additional suitable polyol fatty acid polyesters are esterified epoxide-extended polyols of the general formula  $P(OH)_{A+C} (EPO)_N (FE)_B$  wherein  $P(OH)$  is a polyol, A is from 2 to about 8 primary hydroxyls, C is from about 0 to about 8 total secondary and tertiary hydroxyls,  $A + C$  is from about 3 to about 8, EPO is a  $C_3-C_6$  epoxide, N is a minimum epoxylation index average number, FE is a fatty acid acyl moiety and B is an average number in the range of greater than 2 and no greater than  $A + C$ , as described in U. S. Patent No. 4,861,613 and EP 0324010 A1, incorporated herein by reference. The minimum epoxylation index average number has a value generally equal to or greater than A and is a number sufficient so that greater than 95% of the primary hydroxyls of the polyol are converted to secondary or tertiary hydroxyls. Preferably the fatty acid acyl moiety has a  $C_7-C_{23}$  alkyl chain.

Suitable esterified epoxide-extended polyols include esterified propoxylated glycerols prepared by reacting a propoxylated glycerol having from 2 to 100 oxypropylene units per glycerol with C<sub>10</sub>-C<sub>24</sub> fatty acids or with C<sub>10</sub>-C<sub>24</sub> fatty acid esters, as described in U. S. Patent Nos. 4,983,329 and 5,175,323, respectively, both  
5 incorporated herein by reference. Also suitable are esterified propoxylated glycerols prepared by reacting an epoxide and a triglyceride with an aliphatic polyalcohol, as described in U. S. Patent No. 5,304,665, incorporated herein by reference, or with an alkali metal or alkaline earth salt of an aliphatic alcohol, as described in U. S. Patent No. 5,399,728, incorporated herein by reference. Also suitable are acylated propylene oxide-  
10 extended glycerols having a propoxylation index of above about 2, preferably in the range of from about 2 to about 8, more preferably about 5 or above, wherein the acyl groups are C<sub>8</sub>-C<sub>24</sub>, preferably C<sub>14</sub>-C<sub>18</sub>, compounds, as described in U. S. Patent Nos. 5,603,978 and 5,641,534, both incorporated herein by reference.

Other suitable esterified epoxide-extended polyols include esterified alkoxyated polysaccharides. Suitable esterified alkoxyated polysaccharides are esterified alkoxyated polysaccharides containing anhydromonosaccharide units, more preferred are esterified propoxylated polysaccharides containing anhydromonosaccharide units, as described in U. S. Patent No. 5,273,772, incorporated herein by reference

20 A. Solid Component

1. Esterified Linked alkoxyated glycerins/Esterified epoxide-extended polyols

The polyol fatty acid polyester of the solid component of the present invention will  
25 have a complete melt point of at least 37°C, which is the ordinary body temperature, and more preferably of at least 50°C, and most preferably of at least 60°C, and less than 500 °C.

Suitable polyol fatty acid polyesters of the solid component comprise saturated fatty acid esters having a chain length of at least 16 (C16 or greater), and diversely esterified polyol polyesters having long chain unsaturated fatty acid radicals and short chain fatty acid  
30 radicals, as described hereinafter under "Solid Diversely Esterified Polyol Polyesters." In one embodiment, the solid component used to form the flowable nondigestible oil compositions of the present invention can be a solid component comprising a polyol fatty acid polyester selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof.

35 The following patent documents are incorporated herein by reference and disclose esterified linked alkoxyated polyols and/or esterified epoxide-extended polyols which are suitable for use as the solid component: U.S. Patents 5,273,772 to Cooper; 5,362,894 to

Handweker; 5,374,446 to Ferenz; 5,427,815 to Ferenz; 5,516,544 to Sekula; EPO Patent Document 571,219 published November 24, 1993 in the name of Masten

## 2. Other Solid Polyol Fatty Acid Polyester

As described above, the solid polyol fatty acid polyester of the present invention will  
5 have a complete melt point of at least 37°C, which is the ordinary body temperature, and more preferably of at least 50°C, and most preferably of at least 60°C, and less than 500 °C. In an alternative embodiment, the solid component comprises a solid non-alkoxylated polyol fatty acid polyester selected from (i) a solid saturated polyol polyester, (ii) a solid diversely esterified polyol polyester, (iii) a polyol polyester polymer, and (iv) combinations thereof.

10 Such polyols which are used in the solid component of such alternative embodiments of the present invention preferably contain from about 4 to about 12, more preferably 4 to 8, most preferably 6 to 8, hydroxyl groups. Examples of preferred polyols are sugars (including monosaccharides and disaccharides and trisaccharides) and sugar alcohols, containing from 4 to 11 hydroxyl groups. The trisaccharides raffinose and maltotriose are examples of sugars  
15 which contain 11 hydroxyl groups. The preferred sugars and sugar alcohols are those which contain 4 to 8, more preferably 6 to 8, hydroxyl groups. Examples of those containing four hydroxyl groups are the monosaccharides xylose and arabinose and the sugar alcohol erythritol. Suitable five hydroxyl group-containing polyols are the mono-saccharides galactose, fructose, mannose and glucose, and the sugar alcohol xylitol. A polyol containing  
20 six hydroxyl groups is sorbitol. Examples of disaccharide polyols which can be used include maltose, lactose, and sucrose, all of which contain eight hydroxyl groups. Examples of other suitable polyols are pentaerythritol, diglycerol, triglycerol, alkyl glycosides, and polyvinyl alcohols. One preferred polyol is sucrose.

The average degree of esterification of the solid polyol fatty acid polyesters is of at  
25 least 4 ester groups, i.e., at least 4 of the hydroxyl groups of the polyol are esterified with fatty or other organic acids. Polyol esters that contain 3 or less ester groups are generally digested in (and the products of digestion are absorbed from) the intestinal tract much in the manner of ordinary triglyceride fats or oils, whereas those polyol esters which contain 4 or more ester groups are generally substantially nondigestible and consequently nonabsorbable  
30 by the human body. It is not necessary that all of the hydroxyl groups of the polyol be esterified, but it is preferable that disaccharide molecules contain no more than 3 unesterified hydroxyl groups, and more preferably no more than 2 unesterified hydroxyl groups, so that they are rendered nondigestible. Typically, substantially all (e.g., at least about 85%) of the hydroxyl groups of the polyol are esterified, preferably at least about 95% of the hydroxyl  
35 groups of the polyol are esterified. In the case of sucrose polyesters, typically from about 7 to 8 of the hydroxyl groups of the polyol are esterified.

In one embodiment, the solid polyol fatty acid polyester comprises (i) a solid saturated polyol polyester, and (ii) a solid diversely esterified polyol polyester, the ratio of (i):(ii) being from about 1:20 to about 4:1.

5                    i)        Solid Saturated Polyol Polyester

The solid saturated polyol polyester comprises esters of essentially only, and preferably only, long chain saturated fatty acid radicals which are typically normal and contain at least 14, preferably 14 to 26, and more preferably 16 to 24, and most preferably from 20 to 24, carbon atoms. Particularly preferred are saturated fatty acid radicals of 22  
10 carbon atoms. The long chained saturated radicals can be used in combination with each other in all proportions. The average degree of esterification of these solid saturated polyol polyesters is such that at least 4 of the hydroxyl groups of the polyol are esterified. In the case of sucrose polysaturate esters, from about 7 to 8 of the hydroxyl groups of the polyol are preferably esterified. Typically, substantially all (e.g., at least about 85%, preferably at least  
15 about 95%) of the hydroxyl groups of the polyol are esterified.

Examples of suitable long chain saturated fatty acid radicals include tetradecanoate (myristate), hexadecanoate (palmitate), octadecanoate (stearate), eicosanoate (arachidate), docosanoate (behenate), tetracosanoate (lignocerate), and hexacosanoate (cerotate). Mixed fatty acid radicals from completely or substantially completely hydrogenated vegetable oils  
20 which contain substantial amounts of the desired long chain saturated fatty acids can be used as sources of fatty acid radicals in preparing the solid polyol polyesters useful in the present invention. The mixed fatty acids from such oils should preferably contain at least about 30% (more preferably at least about 50%, most preferably at least about 80%) of the desired long chain saturated fatty acids. Suitable source oils include completely or substantially  
25 completely hydrogenated soybean oil, cottonseed oil, palm oil, peanut oil, corn oil, safflower oil, sunflower oil, sesame oil, low erucic acid rapeseed oil (i.e. canola oil), and high erucic acid rapeseed oil. These oils are typically hydrogenated to an Iodine Value of about 12 or less, and preferably to an Iodine Value of about 8 or less.

Examples of solid polyol polyesters useful as hardstocks in the fat compositions of  
30 the present invention include sucrose octabehenate, sucrose octastearate, sucrose octapalmitate, sucrose heptastearate, xylitol pentastearate, galactose pentapalmitate, and the sucrose hepta- and octaesters of soybean oil and high erucic acid rapeseed oil fatty acids that have been hydrogenated to an Iodine Value of about 8 or less.

35                    The solid saturated polyol polyester generally by itself crystallizes into well defined spherulitic particles from a molten composition at or below the onset crystallization temperature of the solid saturated polyol polyester. The onset crystallization temperature is

that temperature at which a solid polyol fatty acid polyester can first begin to crystallize in the liquid polyol fatty acid polyester. That is, when dissolved in a molten composition comprising the solid saturated polyol polyester in a liquid polyol fatty acid polyester, the solid saturated polyol polyester will tend to form well defined, highly ordered, substantially sphere-shaped crystals, called spherulites, when permitted to cool and crystallize at a first crystallization temperature. In the absence of other solid nondigestible oil components, such as a solid diversely esterified polyol polyester or a polyol polyester polymer, the solid saturated polyol polyester would normally crystallize into spherical-shaped particles called spherulites having a diameter (or maximum particle dimension) of about 3 microns or larger, usually about 3-32 microns, the size being a function of the initial concentration of the solid saturated polyol polyester in the liquid polyol fatty acid polyester and the rate of shearing applied during the crystallization. As will be understood from the processing description herein after, if rapidly cooled and crystallized under shear, a solid saturated polyol polyester will tend to crystallize as discrete non-spherulite particles, typically of less than about 30 microns, preferably less than about 10 microns (although portion of the crystals can form as very small spherulites may also form), as opposed to the above mentioned larger spherulites which readily form at slower rates of cooling (crystallizing) and slower rates of shear.

When co-crystallized with other solid polyol fatty acid polyester components, such as the solid diversely esterified polyol polyesters or polyol polyester polymers, the solid saturated polyol polyester will tend not to form the highly ordered spherulite particles.

In one embodiment, the flowable nondigestible composition comprises a solid component comprising solid saturated polyol polyesters such as sucrose polyol polyesters, and a liquid component comprising a material selected from esterified linked alkoxylated polyols, such as esterified linked alkoxylated glycerines; esterified epoxide-extended polyols; and mixtures thereof.

#### ii) Solid Diversely Esterified Polyol Polyesters

Suitable solid diversely esterified polyol polyesters for use in forming the solid component comprise those polyol polyesters which have their ester group-forming fatty acid radicals selected so that the polyol backbone does not contain all of a single type of ester group. Generally, these polyol polyesters contain two basic types of ester groups. These are (a) ester groups formed from long chain saturated fatty acid radicals, as herein above described, and (b) dissimilar ester groups formed from acid radicals which are "dissimilar" to the long chain saturated fatty acid radicals. When these "dissimilar" fatty acid and/or other organic acid radicals are esterified onto a polyol that contains or will contain long chain saturated fatty acid radicals, they will introduce diverse esterification into the resulting polyol polyester molecule, thereby altering the crystal structure as these molecules pack together



during crystallization. This diverse esterification can be due to differences in length of the ester-forming acid radicals (e.g., short chain versus long chain), or other steric factors, e.g. branched chain versus straight chain, unsaturated chain versus saturated chain, aromatic chain versus aliphatic chain, etc. Polyol polyesters containing these "long chain" and "dissimilar" ester groups are therefore herein called "solid diversely esterified polyol polyesters".

The solid diversely esterified polyol polyesters tend to have "asymmetrical" or irregular molecular structures. It is believed that the asymmetrical structure of these molecules interfere with the normal packing tendency of the symmetrical solid saturated polyol polyester molecules during co-crystallization in the liquid polyol polyester. This interference blocks the usual unrestrained three dimensional growth of the solid saturated polyol polyester molecules and thus induces restrained three dimensional growth or otherwise induces growth in, at most two dimensions, e.g., the formation of relatively thin platelet-like particles.

The dissimilar ester groups are formed from acid radicals selected from long chain unsaturated fatty acid radical, short chain saturated fatty acid radical, and other dissimilar fatty acid radicals, and mixtures thereof. The preferred dissimilar acid radical is a long chain unsaturated fatty acid radical.

The long chain unsaturated fatty acid radicals are typically straight chain (i.e., normal) mono- and di-unsaturates, and contain at least about 12, preferably about 12 to about 26, more preferably about 18 to 22, and most preferably 18 carbon atoms. Examples of suitable long chain unsaturated fatty acid radicals for the solid polyol polyesters herein are lauroleate, myristoleate, palmitoleate, oleate, elaidate, erucate, linoleate, linolenate, arachidonate, eicosapentaenoate, and docosahexaenoate. For oxidative stability, the mono- and/or diunsaturated fatty acid radicals are preferred.

The short chain saturated fatty acid radicals are typically normal and contain 2 to 12, preferably 6 to 12 and most preferably 8 to 12, carbon atoms. Examples of suitable short chain saturated fatty acid radicals are acetate, butyrate, hexanoate (caproate), octanoate (caprylate), decanoate (caprate), and dodecanoate (laurate).

Other dissimilar ester-forming radicals can include fatty-fatty acid radicals having at least one hydroxyl group that is esterified with another fatty or other organic acid. Nonlimiting examples of suitable fatty-fatty acid radicals include 12-hydroxy-9-octadecenoic acid (ricinoleic acid), 12-hydroxy-octadecanoic acid, 9-hydroxy-octadecanoic acid, 9-hydroxy-10, 12-octadecadienoic acid, 9-hydroxy-octadecanoic, 9, 10-dihydroxyoctadecanoic acid, 12, 12-dihydroxyeicosanoic acid, and 18-hydroxy-9, 11, 13-octadecatrienoic acid (kamolenic acid). Ricinoleic acid is a preferred hydroxy-fatty acid. Castor oil is a convenient source of ricinoleic acid. Other sources of hydroxy-fatty acids include hydrogenated castor

oil, strophanthus seed oils, calendula officinalis seed oils, hydrogenated strophanthus seed oils and hydrogenated calendula officinalis seed oils, cardamine impatiens seed oils, kamala oils, mallotus discolor oils, and mallotus claoxyloides oils.

Specific, non-limiting examples of solid polyol fatty acid polyesters of the present invention are sorbitol hexaester in which the acid ester radicals are palmitoleate and arachidate in a 1:2 molar ratio; the octaester of raffinose in which the acid ester radicals are linoleate and behenate in a 1:3 molar ratio; the heptaester of maltose wherein the esterifying acid radicals are sunflower seed oil fatty acids and lignocerate in a 3:4 molar ratio; the octaester of sucrose wherein the esterifying acid radicals are oleate and behenate in a 2:6 molar ratio; and the octaester of sucrose wherein the esterifying acid radicals are laurate, linoleate and behenate in a 1:3:4 molar ratio. A preferred material is sucrose polyester in which the degree of esterification is 7-8, and in which the fatty acid radicals are C<sub>18</sub> mono- and di-unsaturated and behenic, in a molar ratio of about 2:6 to about 1.5:6.5.

In one embodiment, the flowable nondigestible composition comprises a solid component comprising solid diversely esterified sucrose polyol polyesters, and a liquid component comprising a material selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof.

### iii) Solid Polyol Polyester Polymers

Polyol polyester polymers are those formed by polymerizing a polyol polyester monomer to provide a molecule having at least two separate esterified polyol moieties linked by covalent bonds between ester groups of these different polyol moieties. For example, two sucrose octabehenate monomers could be cross-linked between fatty acids to form a polymer. Repeating units of such polyol polyester polymers can be the same or different such that the generic term "polymer" in this context includes the specific term "copolymer". The number of repeating monomer (or co-monomer) units which make up such polyol polyester polymers can range from about 2 to 20, preferably from about 2 to 12. Depending on the method of preparing them, the polyol polyester polymers are frequently oligimers containing from 2 to 4 monomeric units, i.e., are dimers, trimers, or tetramers. The most typical type of polyol polyester polymer for use herein is dimer.

When sucrose is used as the polyol of the polyester polymer, it is preferably completely esterified with fatty acid or other ester group-forming acid radicals. Using sucrose as the polyol, completely esterified sucrose polyester monomer, dimer, and trimer are shown schematically in Figures 1a, 1b, and 1c, respectively. At least about 15%, preferably at least about 45%, more preferably at least about 75%, and most preferably at least about

90% of the hydroxyl groups of the polyol polyester polymer material should be esterified with long chain (C<sub>20</sub> and higher) saturated fatty acid radicals. The sucrose polyester polymers used herein can advantageously have a number average molecular weight of from about 4000 to about 60,000, preferably from about 4000 to about 36,000, more preferably from about 5000 to about 12,000.

Suitable long chain saturated fatty acid radicals for use in preparing the polyol polyester polymers (and its monomers) include those herein before described for preparing the solid diversely esterified polyol polyesters. As in the case of the solid diversely esterified polyol polyesters, mixed fatty acid radicals from source oils which contain substantial amounts of the desired long chain saturated fatty acids (i.e, at least about 30%, preferably at least about 50%, more preferably at least about 80%) can be used as sources of acid radicals in preparing these polyol polyester polymers.

Suitable polyol polyester material which forms the solid nondigestible particles used in the fat compositions herein will generally comprise from about 0% to 99% of the polyol polyester polymer component and from 1% to about 100% of the unpolymerized polyol polyester monomer component, preferably from about 0% to about 90% of the polyol polyester polymer component and from about 10% to about 100% of the monomer component, more preferably from about 0% to 70% of the polymer component and from 30% to about 100% of the monomer component, and most preferably from about 0% to 50% of the polymer component and from 50% to about 100% of the monomer component.

In one embodiment, the flowable nondigestible composition comprises a solid component comprising solid polyol polyester polymers, and a liquid component comprising a material selected from esterified linked alkoxylated polyols, such as esterified linked alkoxylated glycerines; esterified epoxide-extended polyols; and mixtures thereof.

#### iv. Processes for Making Solid Polyol Fatty Acid Polyesters

The solid polyol fatty acid polyesters, including the solid saturated polyol polyester and the solid diversely esterified polyol polyester, the solid polyol polyester polymer and the solid polyol polyester polymer, used in the present invention can be made according to prior known methods for preparing polyesters of polyols. Since the sucrose polyesters are the preferred solid polyol polyesters herein, the invention will be exemplified primarily by these materials.

One such method of preparation is by reacting the acid chlorides of the fatty acids with sucrose. In this method a mixture of the acid chloride or acid anhydrides of the fatty acids can be reacted in one step with sucrose, or the acid chlorides can be reacted sequentially with sucrose. Another preparation method is by the process of reacting methyl esters of the fatty acids with sucrose in the presence of a fatty acid soap and a basic catalyst such as

potassium carbonate. See, for example, U.S. Pat. Nos. 3,963,699, Rizzi et al., issued June 15, 1976; 4,518,772, Volpenhein, issued May 21, 1985; and 4,517,360, Volpenhein, issued May 14, 1985, and U.S.S.N. 417,990, Letton, filed October 6, 1989, all incorporated herein by reference. Methods for preparing polyol polyester polymers are described in U.S. Patent 5,451,416, issued Sept. 19, 1995 (Johnston et. al.), the disclosure of which is incorporated herein by reference.

When using the methyl ester route for preparing the solid polyol polyesters herein, the fatty acid methyl esters are blended in the desired ratio and reacted with sucrose by transesterification to obtain the sucrose esters of mixed unsaturated/saturated or saturated fatty acids. In a preferred way of practicing the methyl ester process, five moles of the blended saturated/unsaturated or saturated methyl esters are reacted with sucrose in a first stage at 135°C to obtain partial esters of sucrose. An additional nine moles of the blended esters are then added and the reaction continued at 135°C under reduced pressure until the desired degree of esterification has been attained.

When two or more of the solid saturated polyol polyester, solid diversely esterified polyol polyester and solid polyol polyester polymer are used as the solid polyol polyester, then can be made and incorporated separately into the nondigestible oil composition, or alternatively, they can be made and mixed together and incorporated into the nondigestible oil composition. In a preferred process where the solid polyol fatty acid polyester comprises the solid saturated polyol polyester and the solid diversely esterified polyol polyester, the two solid polyesters are made simultaneously in the same polyol esterification preparation. The preferred method of making the solid polyol fatty acid polyester is to esterify the polyol with a mixture of long chain saturated fatty acid lower alkyl (preferably methyl) esters, and dissimilar fatty acid alkyl (preferably methyl) esters selected from short chain saturated fatty acid alkyl esters, long chain unsaturated fatty acid alkyl esters, dissimilar acid alkyl esters, and mixtures thereof. When prepared in the same preparation, the esterification of the polyol hydroxy sites by the mixture of long chain saturated fatty acid radicals and dissimilar fatty acid radicals will occur substantially randomly. In order to ensure that a portion of the solid polyol polyesters are esterified only with long chain saturated fatty acid radicals, it is generally required to include proportionally more of the long chain saturated fatty acid radicals as compared to the dissimilar fatty acid radicals. For example, sucrose has 8 hydroxy sites which are capable of being esterified. Depending upon the chain lengths of the esters and other processing conditions, in order to obtain a significant (10% or greater) amount of sucrose octasaturate and sucrose heptasaturate polyester from the reaction of sucrose with a mixture of long chain saturated fatty acid methyl esters and long chain unsaturated fatty acid methyl esters, a molar ratio of long chain saturated esters to long chain unsaturated esters of about 6:2 or more will be needed. As an example of a particularly

preferred solid polyol polyester, a molar ratio of 6.5:1.5 of C22 saturated fatty acid ester to cottonseed oil (about 73% unsaturated) ester is used, resulting in about 20 % on a molar basis of sucrose octasaturate and sucrose heptasaturate polyester (as the solid saturated polyol polyester), with the remaining polyesters (about 80% on a molar basis) being  
5 substantially octa- and hepta-substituted and having a mixture of long chain saturated fatty acid radicals and long chain unsaturated fatty acid radicals (as the diversely esterified polyol polyester). Increasing the ratio of long chain saturated radicals to long chain unsaturated radicals will result in a higher proportion of the solid polyesters being converted to solid saturated polyol polyesters; conversely decreasing the ratio of long chain saturated fatty acid  
10 radicals to long chain unsaturated fatty acid radicals will tend to result in a lower proportion of the solid polyesters being converted to the solid saturated polyol polyesters.

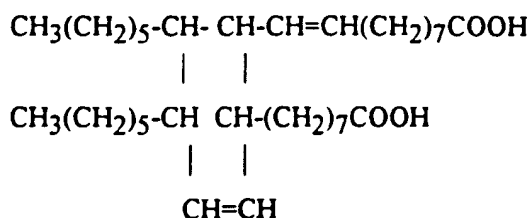
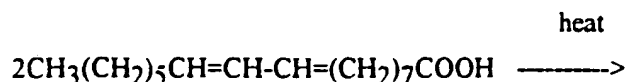
Mixed fatty acid radicals from source oils which contain substantial amount of the desired unsaturated or saturated acids can be used as the fatty acid radicals to prepare compounds of the invention. The mixed fatty acid radicals from the oils should contain at  
15 least about 30% (preferably at least about 50%, most preferably at least about 80%) of the desired unsaturated or saturated acids. For example, rapeseed oil fatty acid radicals or soybean oil fatty acid radicals can be used instead of pure C<sub>12</sub>-C<sub>26</sub> unsaturated fatty acids. Hardened (i.e., hydrogenated) high erucic rapeseed oil fatty acids can be used instead of pure C<sub>20</sub>-C<sub>26</sub> saturated fatty acids. Preferably the C<sub>20</sub> and higher acids (or their derivatives -  
20 e.g., methyl esters) are concentrated, for example by distillation. The fatty acids from palm kernel oil or coconut oil can be used as a source of C<sub>8</sub> to C<sub>12</sub> acids. An example of the use of source oils to make solid polyol polyesters of the invention is the preparation of solid sucrose polyester, employing the fatty acids of high oleic sunflower oil and substantially completely hydrogenated high erucic rapeseed oil. When sucrose is substantially completely  
25 esterified with a 1:3 by weight blend of the methyl esters of the fatty acids of these two oils, the resulting sucrose polyester will have a molar ratio of unsaturated C<sub>18</sub> acid radicals to C<sub>20</sub> and higher saturated acid radicals of about 1:1 and 28.6 weight percent of the total fatty acids in the polyester will be C<sub>20</sub> and C<sub>22</sub> fatty acids. The higher the proportions of the desired unsaturated and saturated acids in the fatty acid stocks used in making the solid  
30 polyol polyester, the more efficient the ester will be in its ability to bind liquid oils.

One way to prepare this material is by synthesizing monomeric polyol polyester according to known polyol esterification, transesterification and/or interesterification methods and by then polymerizing these monomers. The polymerization step can be initiated and promoted by any of a number of well known methods, including, but not limited to,  
35 photochemical reactions and reactions with transition metal ions, heat or free radical initiators such as di-tert-butyl peroxide.

Alternatively, polyol polyester polymers can be prepared directly by esterifying and/or interesterifying the polyol material with polybasic polymerized fatty acids or their derivatives. For example, the polyol polyester polymers could be prepared by reacting the acid chlorides or acid anhydrides of the desired esterifying polymer acids with sucrose, preferably using a sequential esterification process in the manner described herein before for the preparation of diversely esterified polyol polyesters. The polyol polyester polymers could also be prepared by reacting the methyl esters of the desired polymer acids with sucrose in the presence of a fatty acid soap and a basic catalyst such as potassium carbonate in the manner described herein before for the preparation of diversely esterified polyol polyesters.

When using the foregoing methods for preparing sucrose polyester material containing both unpolymerized and polymerized fatty acid groups, the molar ratio of unpolymerized to polymerized fatty acids in the resulting sucrose material can range from about 2:6 to about 4:4.

When using the acid chloride or methyl ester procedures herein before described to esterify the polyol with already polymerized fatty acids, a wide variety of pre-polymerized fatty acid materials can be used. One such class of suitable polymerized fatty acids comprises long-chain, aliphatic, dibasic acids having from about 28 to about 44 carbon atoms in their molecules. They are generally formed from unsaturated fatty acids having from about 14 to about 22 carbon atoms which can be polymerized. For example linoleic acid can be polymerized by heating to form linoleic acid dimer as follows:



Common examples of polymerizable acids of this type are those containing two or more double bonds (polyunsaturated acids) such as the octadecadienoic acids containing two double bonds, for example, the above-mentioned linoleic acid, and the octadecatrienoic acids containing 3 double bonds, for example, linolenic and eleostearic acids. Other common polymerizable polyunsaturated acids having from about 14 to about 22 carbon which can be used to esterify polyols and thereby form the polyol polyester polymers herein are

octadecatrienoic acid (e.g., licanic acid), actadectetraenoic acid (e.g., parinaric acid), eicosadienoic acid, eicostetraenoic acid (e.g., arachidonic acid), 5,13-docosadienoic acid and clupanodonic acid. Monounsaturated fatty acids, such as oleic, elaidic and erucic acids, can also be used in preparing suitable long chain fatty acid dimers which in turn can then be used to form the solid polyol polyester polymer particles used in the present invention.

Mixed fatty acid radicals from source oils which contain substantial amounts of the desired polymerizable polyunsaturated or monounsaturated fatty acids can be used as sources of acid radicals in preparing the polyol polyester polymer materials used to form the solid particles used in the present invention. The mixed fatty acids from such source oils should preferably contain at least about 30% (more preferably at least about 50%, most preferably at least about 80%) of the desired polymerizable polyunsaturated or monounsaturated fatty acids.

Illustrative of natural sources which are rich in linoleic acid are soybean oil, cottonseed oil, peanut oil, corn oil, sesame seed oil, sunflower seed oil, safflower oil, linseed oil and perrilla oil. Oiticica oil is a particularly good source of licanic acid and tung oil contains a high concentration of eleostearic acid. Fish oils, such as herring, menhaden, pilchard, salmon and sardine oil are also suitable sources of polymerizable acids, particularly the higher fatty acids such as arachidonic and clupanodonic acids. Other oils such as tall oil, dehydrated castor oil, olive oil and rapeseed oil also contain significant proportions of suitable unsaturated acids. For example, olive oil is rich in oleic acid and rapeseed oil is rich in erucic acid.

Preferred polybasic polymerized fatty acids and fatty acid derivatives for use in preparing polymer-containing polyol polyesters include dibasic acids produced by dimerization of the fatty acids or fatty acid lower esters derived from polyunsaturated vegetable oils such as soybean oil or cottonseed oil or from animal fats such as tallow.

All of the foregoing types of polybasic polymerized fatty acids may themselves be made by a variety of methods known to those skilled in the art. (See Lutton; U.S. Patent 3,353,967; Issued November 21, 1967, Goebel; U.S. Patent 2,482,761; Issued September 27, 1949, Harrison et al; U.S. Patent 2,731,481; Issued January 17, 1956 and Barrett et al; U.S. Patent 2,793,219; Issued May 21, 1957, all of which are incorporated herein by reference.)

As noted, a mixture of both polymerized and unpolymerized polyol polyester material can be prepared by reacting the polyol with both polymerized and unpolymerized esterifying fatty acids or fatty acid derivatives. In a preferred method for preparing particularly desirable solid sucrose polyester material comprising sucrose polyester polymers, fractionated or unfractionated high erucic acid rapeseed (HEAR) methyl esters are partially polymerized, hardened and then reacted with sucrose. Another method of making these especially desirable solid sucrose polyesters is to make liquid sucrose polyester material esterified with fatty acid

groups of high erucic acid rapeseed oil by a conventional process, to then partially polymerize the resulting liquid sucrose polyester material, and to then harden the resulting polymerized material.

#### B. Liquid Component:

- 5           The flowable nondigestible oil composition of the present invention also comprises a liquid component having a complete melting point below about 37°C, which liquid component includes minimal or no solids at body temperature (98.6 F, 37 C).

##### 1. Liquid Esterified Linked alkoxyated glycerins/Esterified epoxide-extended polyols

- 10           In one embodiment, the liquid component used to form the flowable nondigestible oil compositions of the present invention can be a liquid component comprising a material selected from esterified linked alkoxyated polyols, such as esterified linked alkoxyated glycerines; esterified epoxide-extended polyols; and mixtures thereof.

- 15           The following patent documents are incorporated herein by reference and disclose esterified linked alkoxyated polyols and/or esterified epoxide-extended polyols which are suitable for use as the liquid component: U.S. Patents 4,861,613 to Pollard; 4,983,329 to Cooper; 5,175,323 to Cooper; 5,273,772 to Cooper; 5,304,665 to Cooper; 5,399,728 to Cooper; 5,512,213 to Cooper; 5,603,978 to White; 5,641,534 to White; EPO Patent Documents 325,010 published July 26, 1989 in the name of White et al.; 667,105 published 20   August 16, 1995 in the name of Ziegert et al.; PCT Publication WO 97/222260.

##### 2. Other Liquid Polyol Fatty Acid Polyester

- 25           Other suitable liquid nondigestible edible oils for use herein include liquid, non-alkoxyated polyol polyesters (see Jandacek; U.S. Patent 4,005,195; issued January 25, 1977); liquid esters of tricarballic acids (see Hamm; U.S. Patent 4,508,746; issued April 2, 1985); liquid diesters of dicarboxylic acids such as derivatives of malonic and succinic acid (see Fulcher, U.S. Patent 4,582,927; issued April 15, 1986); liquid triglycerides of alpha-branched chain carboxylic acids (see Whyte; U.S. Patent 3,579,548; issued May 18, 1971); 30   liquid ethers and ether esters containing the neopentyl moiety (see Minich; U.S. Patent 2,962,419; issued Nov. 9, 1960); liquid fatty polyethers of polyglycerol (See Hunter et al; U.S. Patent 3,932,532; issued Jan. 13, 1976); liquid alkyl glycoside fatty acid polyesters (see Meyer et al; U.S. Patent 4,840,815; issued June 20, 1989); liquid polyesters of two ether linked hydroxypolycarboxylic acids (e.g., citric or isocitric acid) (see Huhn et al; U.S. Patent



4,888,195; issued December 19, 1988); as well as liquid polydimethyl siloxanes (e.g., Fluid Silicones available from Dow Corning). All of the foregoing patents relating to the liquid nondigestible oil component are incorporated herein by reference.

Preferred liquid nondigestible oils are the liquid polyol polyesters that comprise liquid  
5 sugar polyesters, liquid sugar alcohol polyesters, and mixtures thereof. The preferred sugars and sugar alcohols for preparing these liquid polyol polyesters include erythritol, xylitol, sorbitol, and glucose, with sucrose being especially preferred. The sugar or sugar alcohol starting materials for these liquid polyol polyesters are preferably esterified with fatty acids containing from 8 to 22 carbon atoms, and most preferably from 8 to 18 carbon atoms.  
10 Suitable naturally occurring sources of such fatty acids include corn oil fatty acids, cottonseed oil fatty acids, peanut oil fatty acids, soybean oil fatty acids, canola oil fatty acids (i.e. fatty acids derived from low erucic acid rapeseed oil), sunflower seed oil fatty acids, sesame seed oil fatty acids, safflower oil fatty acids, fractionated palm oil fatty acids, palm kernel oil fatty acids, coconut oil fatty acids, tallow fatty acids and lard fatty acids.

15 The nondigestible polyol polyesters that are liquid are those which have minimal or no solids at body temperatures (i.e., 98.6°F, 37°C). These liquid polyol polyesters typically contain ester groups having a high proportion of C<sub>12</sub> or lower fatty acid radicals or else a high proportion of C<sub>18</sub> or higher unsaturated fatty acid radicals. In the case of those liquid polyol polyesters having high proportions of unsaturated C<sub>18</sub> or higher fatty acid radicals, at  
20 least about half of the fatty acids incorporated into the polyester molecule are typically unsaturated. Preferred unsaturated fatty acids in such liquid polyol polyesters are oleic acid, linoleic acid, and mixtures thereof.

The following are nonlimiting examples of specific liquid polyol polyesters suitable  
25 for use in the present invention: sucrose tetraoleate, sucrose pentaoleate, sucrose hexaoleate, sucrose heptaoleate, sucrose octaoleate, sucrose hepta- and octaesters of unsaturated soybean oil fatty acids, canola oil fatty acids, cottonseed oil fatty acids, corn oil fatty acids, peanut oil fatty acids, palm kernel oil fatty acids, or coconut oil fatty acids, glucose tetraoleate, the glucose tetraesters of coconut oil or unsaturated soybean oil fatty acids, the mannose  
30 tetraesters of mixed soybean oil fatty acids, the galactose tetraesters of oleic acid, the arabinose tetraesters of linoleic acid, xylose tetralinoleate, galactose pentaoleate, sorbitol tetraoleate, the sorbitol hexaesters of unsaturated soybean oil fatty acids, xylitol pentaoleate, and mixtures thereof.

The liquid polyol polyesters suitable for use in the compositions herein can be  
35 prepared by a variety of methods known to those skilled in the art. These methods include: transesterification of the polyol (i.e. sugar or sugar alcohol) with methyl, ethyl or glycerol esters containing the desired acid radicals using a variety of catalysts; acylation of the polyol

with an acid chloride; acylation of the polyol with an acid anhydride; and acylation of the polyol with the desired acid, per se. (See, for example, U.S. Patent Nos. 2,831,854, 3,600,186, 3,963,699, 4,517,360 and 4,518,772, all of which are incorporated by reference. These patents all disclose suitable methods for preparing polyol polyesters.)

5    C. Other Shortening Ingredients

So long as they do not interfere with the formation of the flowable nondigestible oil, the flowable nondigestible oil compositions may also comprise other shortening ingredients. Various additives can be used herein provided they are edible and aesthetically desirable and  
10   do not have any detrimental effects on the shortenings. These additives include edible, digestible oils and hardstock, fat-soluble vitamins, flavorings and seasonings, emulsifiers, anti-spattering agents, chelating agents, anti-sticking agents, anti-oxidants, anti-foaming agents (for frying applications) or the like.

D.   Formation of Stiffened Nondigestible Oil

15       The nondigestible oil composition described herein is capable of crystallizing from a molten liquid form to a stiffened nonflowable oil form when the nondigestible oil composition is rapidly cooled from the molten temperature to the crystallization temperature of the solid polyol polyester, or less (for example, to body temperature, about 37°C) under substantially quiescent conditions. This stiffened nonflowable nondigestible oil comprises the liquid  
20   nondigestible oil portion retained substantially completely within the crystalline matrix of crystallized solid polyol fatty acid polyester, thereby providing the desired passive oil loss control of the nondigestible oil. The composition and method of making of the food composition should be selected to provide the sufficiently rapid cooling of the nondigestible oil from a molten temperature to a lower temperature substantially in the absence of shearing  
25   of the food composition, such that the solid polyol fatty acid polyester has crystallized into the desired crystalline form which provides the desired passive oil loss control. Generally, this cooling rate from the onset crystallization temperature of the highest melting solid polyol fatty acid polyester to the crystallization temperature (of the lowest melting solid polyol fatty acid polyester component) is greater than about 0.5 °C/min, more preferably greater than  
30   about 2.5 °C/min, and most preferably greater than 25°C/min. In the case of a polyol polyester polymer, which can form the desired crystal structure for passive oil loss control at much slower cooling rates, a cooling rate of greater than about 0.03 °C/min. under the quiescent conditions is generally sufficient to form the desired crystal structure.

When a nondigestible oil composition comprising a solid polyol fatty acid polyester  
35   containing any one or a combination of a solid saturated polyol polyester, a solid diversely esterified polyol polyester, and a polyol polyester polymer, begin to crystallize (or co-

crystallize) in the liquid polyol polyester, the crystals (or co-crystals) initially appear as discrete, unaggregated entities, suspended in the liquid polyol fatty acid polyester. Under quiescent cooling conditions, such as when the molten nondigestible oil has been processed into food products via baking or frying, these discrete unaggregated entities can grow as crystallization continues, and begin to cluster together to form small aggregates of at least 3 microns, dispersed in the liquid nondigestible oil. These small aggregate clusters of particles can develop in a variety of forms and shapes, including spherical, platelet-like, filament-like or rod-like, or combinations of these various shapes, but are typically spherical or platelet-like. Thinner aggregate particles, referred to as platelets, are preferred from the standpoint of providing more efficient passive oil loss control of the liquid polyol polyester component of the nondigestible oil compositions herein. These platelet particles preferably have a thickness of about 0.1 micron or less, more preferably about 0.05 micron or less. As the crystallization continues, the platelets continue to grow and to cluster together to form a larger aggregate particle that is porous in character and thus capable of entrapping significant amounts of the liquid polyol polyester. It is believed that this porous structure and its concomitant ability to entrap large amounts of liquid polyol polyester is why these larger aggregated, platelet-like particles can provide very effective and efficient passive oil loss control, and results in a stiffened, nonflowable nondigestible oil.

## 20 II. Process for Making a Flowable Nondigestible Oil Composition:

The present invention also provides a process for making a flowable nondigestible oil composition comprising a liquid component having a complete melt point less than 37°C, and a solid component having a complete melt point of at least about 37°C. The process comprises the steps of:

- a) providing a mixture comprising the liquid component and the solid component, wherein at least one of the liquid component and the solid comprises a material selected from esterified linked alkoxylated polyols, such as esterified linked alkoxylated glycerines; esterified epoxide-extended polyols; and mixtures thereof;
- 30 b) melting the mixture of the liquid component and the solid component;
- c) crystallizing at least a substantial portion of the solid component; and
- d) shearing the mixture of the liquid component and the solid component during the step of crystallizing, thereby forming at least a substantial portion of the solid component into crystallized particles.

35

According to one embodiment, the process comprises the steps of melting completely the mixture containing the solid component, rapidly cooling the melted mixture to a crystallization temperature, thereby rapidly crystallizing at least a substantial portion of the solid component, and shearing the mixture during the step of crystallizing to form the flowable nondigestible oil composition. Optionally, following the crystallizing and shearing steps, the process can include one or both of the following steps: 1) the step of tempering the crystallized nondigestible oil composition for a time sufficient to substantially completely crystallize all of the solid component, and/or 2) the step of adding a stabilizing amount of a diluent liquid, typically a liquid polyol fatty acid polyester, to the crystallized nondigestible oil composition, or both steps.

The process of the present invention for making a flowable nondigestible oil typically requires at least about 5 minutes and generally no more than about 3 hours, preferably at least about 5 minutes and generally no more than about 2 hours, more preferably at least about 10 minutes and no more than about 1 hour, and most preferably at least about 15 minutes and no more than about 30 minutes.

Without the invention being bound by any theory of crystallization described herein, it is understood that crystallization of the solid component occurs kinetically. As with any kinetic reaction, a dynamic equilibrium can be achieved wherein the reaction may appear to have halted. Then, by changing the conditions, the reaction can be made to proceed forward, or even to reverse. In the same way, the solid component can crystallize under a condition until a dynamic equilibrium is achieved. The dynamic equilibrium can exist wherein a portion of a solid component is still dissolved in the liquid component while the preponderance has been crystallized. The rate at which a solid component will crystallize depends upon several factors, such as, the molecular composition of the solid component, the concentration of the solid component, the proportion of solid component already crystallized to that remaining dissolved in the liquid component, and the temperature differential between the onset crystallization temperature of the solid component and the temperature of crystallization.

At the onset of crystallization, the solid component will initially crystallize at a high crystallization rate. This crystallization rate slows with time, eventually (ideally) to a rate of zero. Then, when the mixture of the solid and liquid components is further cooled to a lower temperature the equilibrium is shifted such that, for instance, it is possible that additional solid polyol fatty acid polyester can crystallize from the liquid polyol polyester. While the proportion of solid polyol fatty acid polyester which will crystallize with an incremental reduction in temperature is generally low, it is believed that additional crystallizing solid polyol fatty acid polyester will, in the absence of shearing, tend to crystallize as discrete, unaggregated entities suspended in the liquid polyol fatty acid polyester or onto other aggregate particles. The discrete unaggregated entities may begin to cluster together to form

small aggregates, typically up to several microns in size. However, in the presence of applied shear, these unaggregated entities generally do not form into aggregate particles, and any aggregate particles that might form do not generally continue to cluster into a large matrix of crystal aggregate, thereby promoting the flowability of the nondigestible oil.

5       The flowable nondigestible oil composition of the present invention can be processed using crystallization and mixing equipment that is commonly employed to crystallize fats. Both batch and continuous processing systems and equipment can be used, though a continuous system is generally preferred. The general requirement of the system is to be capable of rapidly cooling the molten polyol polyester component to the crystallization  
10       temperature range, and crystallizing at least a substantial portion of the solid polyol fatty acid polyester, most preferably while simultaneously shearing the composition sufficiently to form the flowable nondigestible oil composition.

A.     Melting of the Nondigestible Oil Composition

15       The first step of the process of the present invention comprises melting the solid component in the liquid component at a temperature above the temperature where the last amount of the solid component is melted into the liquid. Preferably, the composition is raised to a temperature at least 10 °C above the complete melt temperature of the solid component.

20       In the molten state, the nondigestible oil compositions are generally transparent and clear. It will be observed that as the solid component begins to crystallize (at and below the onset crystallization temperature), the liquid component begins to become turbid and clouded. The "onset crystallization temperature" for the solid components described herein can be determined by the method described below in the Analytical section.

B.     Crystallization of the Solid Component

25       The next step of the process comprises rapidly crystallizing at least a substantial portion of the solid component, defined as at least more than 50% by weight, and preferably more than 80%, more preferably more than 95%, and most preferably more than 99%. This step can comprise the steps of reducing the temperature of the molten mixture of the melted solid component and the liquid component to a crystallization temperature of the solid component, and holding the mixture at the crystallization temperature for a time sufficient to  
30       crystallize the substantial portion of the solid component.

The crystallization temperature is preferably within a crystallization temperature range of from about the onset crystallization temperature of the solid component, down to about 25°C, preferably down to about 10°C. Where the solid component contains two or

more distinct materials, such as two distinct solid polyol fatty acid polyester materials having different onset melting temperatures, preferably the crystallization temperature is below the lowest onset temperature thereof, and preferably at least about 5°C, more preferably at least about 10°C, below the lowest onset crystallization temperature. Most preferably, the crystallization temperature ( or lowest crystallization temperature if there are multiple solid materials) is within the temperature range of the storage conditions for the flowable nondigestible oil, such storage temperature range typically being about 15°C to about 40°C, and more particularly about 25°C to about 30°C. It should be understood that the rate of crystallization of the solid component will be higher as the crystallization temperature is reduced lower below the onset crystallization temperature of the solid component.

The step of rapidly crystallizing the substantial portion of the solid component can be completed in less than about 30 minutes, preferably in less than about 5 minutes, and more preferably in less than about 30 seconds, and most preferably in less than about 15 seconds. Generally about 5 seconds to about 30 seconds are needed depending upon the type of equipment used. While the step can be completed within a period of time of more than 30 minutes, such additional time is understood to provide no particular additional benefits.

The process also comprises the step of shearing during the step of crystallizing the solid component at the crystallization temperature. By applying shear to the composition during the crystallization, the solid component is encouraged to crystallize into discrete crystals and unaggregated crystal platelets. By shearing while the crystallization is occurring, the resulting discrete and unaggregated crystals can be inhibited from growing to a size that might be large enough to separate from the liquid phase. It is also believed that the small crystal platelets may aggregate into small aggregate particles, but that the shearing inhibits the small aggregate particles from further clustering into larger aggregate particles which can begin to stiffen the composition. During the crystallizing step, shear is imparted to the mixture at from about 400 sec<sup>-1</sup> to about 8000 sec<sup>-1</sup>, more preferably at from about 500 sec<sup>-1</sup> to about 6000 sec<sup>-1</sup>.

The crystallizing step can be conducted in such equipment as a swept-wall, scraped-wall, or screw-type heat exchanger or equivalent, scraped wall agitated reactors, plate and frame heat exchangers, and tube and shell heat exchangers. Such equipment in general cools the composition at a rate of from about 0.4°C/min. to 300°C/min., more preferably from about 0.8°C/min. to about 150°C/min. Examples of such heat exchangers include Cherry Burrell Votator, Girdler "A" units, a Sollich Turbo Temperer, and a Groen Model #DR(C) used for margarine and shortening manufacture, and Aasted chocolate tempering units. A preferred unit is the Votator unit which consists of a steel shaft rotating in a tube which is cooled externally by a coolant. The rotating shaft is fitted with scraper blades which press against the cool inner surface at high rotation speeds, continuously scraping the crystallizing

composition from the inner surface of the tube. References to these conventional units include: Greenwell, B. A., J. Amer. Oil Chem. Soc., March 1981, pp. 206-7; Haighton, A. J., J. Amer. Oil Chem. Soc., 1976, Vol. 53, pp. 397-9; Wiedermann, L. H. J. Amer. Oil Chem. Soc., Vol. 55, pp. 826-7; Beckett, S. T., editor, Industrial Chocolate Manufacture and Use, Van Nostrand Reinhold, New York, 1988, pp. 185-9. All of these publications are  
5 incorporated herein by reference.

A scraped wall heat exchanger is a preferred apparatus for rapidly reducing the temperature and providing crystallization under high shear, typically at temperature reduction rates of about 8-300°C/min., and preferably about 100-300°C/min. The temperature of the  
10 coolant used for this crystallizing step in this equipment is sufficiently low to quickly cool the mixture, but not so low so as to cause a significant amount of plating out of the solid component onto the chilled surfaces of the apparatus. Typically the coolant temperature is in the range of from about -23°C to about 20°C, more preferably in the range of from about -6.7°C to about 7°C. Typical coolants include liquid ammonia, brine, and other refrigerants.

15 The melted mixture can also be pre-cooled before entering the scraped wall heat exchanger, to a temperature not far above the onset crystallization temperature of the solid component, using a separate heat exchanger.

In general, the rate of shearing to be applied to the composition during the crystallization step should be commensurate with the rate of crystallization of the solid  
20 component. That is, for example, when the crystallization temperature is set well below the onset crystallization temperature such that the rate of crystallization is very high; then higher rates of shearing are needed to form the desired crystal platelet particles. Of course, if the crystallization rate greatly exceeds the shearing rate, such that large aggregate particles are formed in the composition, the shearing can be continued after crystallization has slowed or  
25 stopped to effect a reduction in the large aggregate particles and a resulting more flowable composition, by the breaking and tearing of the large aggregate particles by the force of shear.

Following the step of rapidly crystallizing and shearing the mixture to form the discrete and unaggregated crystal particles, it is preferred to continue shearing the crystallized  
30 composition at the crystallization temperature for a time sufficient for crystallization of the solid component to come substantially to completion, and to allow the solid component to complete crystallization to the discrete and unaggregated crystal particles. The continued shearing step serves to disrupt the formation of larger aggregate particles and any three-dimensional crystalline matrix that otherwise can form from the larger aggregate particles in  
35 the absence of the shearing. Such continued shearing preferably avoids creating any dead zones in the mixing vessel which might resulting in a localized stiffened composition. Typically the continued shearing is done for at least about 2 seconds, preferably for about 5

minutes, and more preferably for at least about 10 minutes. Generally no more than about 2 hours, preferably about no more than 1 hour, more preferably no more than about 30 minutes, is required for the continued shearing step.

In the continued shearing step, generally less shear is needed in comparison with that used during the crystallization step. Generally during the continued shearing step, shear rates range from about  $10 \text{ sec}^{-1}$  to about  $8000 \text{ sec}^{-1}$ . Preferred types of apparatus for carrying out the continued shearing step include any agitated, jacketed vessel capable of being operated such that preferably air can be excluded from incorporation into the polyol polyester composition, and the temperature of the composition can be suitably controlled. An example of a suitable scraped-wall, jacketed, open tank mixer is a Krueter temper kettle (Beckett, pp. 183-4). In addition, it is possible to carry out the conditioning step in two or more separate pieces of agitated, heat exchanger equipment. Another mechanical devices that can be used for the continued shearing of the crystallized polyol polyester is a Ross 410 X-3 or a Readco twin screw mixer.

The continued shearing step can also be accomplished using non-mechanical mixing devices such as static mixers, consisting of a pipe section having a plurality of mixing elements contained in a series therein. Turbulence and shear are imparted to the product as it passes through stationary mixing blades within the pipe. Manufacturers of in-line static mixer include Komax and Lightrii.

It is also possible to carry out both the crystallizing step and any continued shearing step in a single piece of equipment, such as, for example, in a turbo temperer such as a Sollich Turbo Tempering column.

### C. Tempering

The process of the present invention can optionally include a tempering step. The tempering step comprises reducing the temperature of the crystallized mixture to a tempering temperature that is less than the intended minimum handling and storage temperature of the flowable nondigestible composition, and holding the composition at the tempering temperature for a time sufficient to substantially complete crystallization. A tempering step can advantageously be employed when the crystallization temperature of the crystallizing step is above the intended storage temperature of the flowable nondigestible composition. The tempering step is usually not required when the crystallization temperature is itself below the intended storage temperature. The tempering temperature is preferably at least  $5^{\circ}\text{C}$ , more preferably at least  $10^{\circ}\text{C}$ , below the intended ambient handling/storage temperature of the flowable nondigestible composition. Typically, the tempering temperature is from about  $5^{\circ}\text{C}$  to about  $25^{\circ}\text{C}$ , preferably about  $5^{\circ}\text{C}$  to about  $15^{\circ}\text{C}$ .



In order to prevent the aggregation of crystallized particles during the tempering step, shear mixing should be applied to the mixture. In general the tempering step will take from about 2 minutes to about 2 hours, preferably from about 2 minutes to about 1 hour, more preferably about 5 minutes to about 20 minutes. The amount of shearing that is typically  
5 provided in the tempering step will be substantial the same as that provided during the crystallization step, though preferably it is at least about  $1 \text{ sec}^{-1}$ , and preferably about  $25 \text{ sec}^{-1}$  to about  $50 \text{ sec}^{-1}$ . As with the continued shearing, the tempering step should avoid creating any dead zones in the mixing vessel which might result in a localized stiffened composition.

10 Following the tempering step, the flowable nondigestible composition is preferably raised in temperature to the ambient handling/storage temperature.

#### D. Diluent Addition

The process of the present invention can also optionally include a step of adding an amount of, and preferably a stabilizing amount of, a diluent liquid to the crystallized mixture in order  
15 to form, and preferably to ensure the stability of, the resulting flowable nondigestible composition. The principle of adding a diluent liquid is to increase incrementally the solubility of the solid component into the liquid component, thereby promoting a more flowable composition. Preferably the diluent liquid is added after the crystallization temperature has been reduced to the ambient storage temperature, even more preferably after  
20 any tempering step. The addition of the diluent can reduce, and preferably stop, the driving force which promotes crystallization of the solid out of solution, and can even result in some amount of re-solubilizing of crystallized solid polyol polyester back into the liquid phase. The diluent is added in an amount, relative to the amount of the processed nondigestible oil after tempering, generally at about 10:1 to about 0.01:1, preferably about 2:1 to about  
25 0.01:1, more preferably about 1:1 to about 0.05:1, and most preferably about 0.5:1 to about 0.1:1. The temperature of the diluent liquid is from about  $5^{\circ}\text{C}$  to about  $50^{\circ}\text{C}$ , more preferably about  $10^{\circ}\text{C}$  to about  $25^{\circ}\text{C}$ , when it is added to the crystallized mixture. The temperature of the diluent liquid will depend upon the amount of diluent liquid used, the preferred storage temperature of the flowable nondigestible oil, and other factors that will be  
30 understood by one skilled in the art.

The liquid diluent can comprise liquid polyol polyesters, including alkoxyated and non-alkoxyated polyol polyesters. A preferred diluent is a liquid having the same composition as the liquid component used to form the flowable nondigestible composition, however, any suitable combination of solid component, liquid component, and liquid diluent  
35 can be used. For instance, if the liquid component comprises a liquid esterified linked alkoxyated polyol, the liquid diluent can comprise the same liquid esterified linked

alkoxylated polyol, a different esterified linked alkoxylated polyol, or a non-alkoxylated liquid polyol, such as sucrose polyester. Other diluents can be other edible oils, preferably nondigestible oils, which are miscible with the liquid component of the flowable nondigestible composition, and are generally lipophilic.

5

If the flowable nondigestible oil composition is permitted to set without any circulation or stirring for an extended period of time, it is possible that minor temperature fluctuations could result in an incremental crystallization of remaining solid component in the liquid component, which could result in a thickening and stiffening of the composition.

10 Application of additional shear, therefore, would serve to break up any larger aggregate particles that may have formed from the clustering of small aggregate particles, thereby reducing the Consistency of the composition.

The step of adding the diluent liquid to the crystallized mixture can be before any continued shearing of the crystallized mixture or after any continued shearing step. The  
15 adding of the diluent liquid before the continued shearing step reduces the time needed for the continued shearing.

### III. Temperature Sensitive Food Additives

20 The flowable nondigestible oil composition can further comprise temperature-sensitive food additives, including fat-soluble and other vitamins, flavorings, and seasonings. The food additives can be added either as a particulate or as a liquid. When adding as a particulate, the particulate food additive can be added to the final flowable nondigestible oil, or added during the crystallization of the compositions at a step where the temperature does  
25 not adversely effect the efficacy of the additive.

The present flowable nondigestible oil compositions can also be fortified with vitamins and minerals, particularly the fat-soluble vitamins. The fat-soluble vitamins include vitamin A, vitamin D, vitamin K, and vitamin E. (See U.S. Pat. 4,034,083 (Mattson) issued July 5, 1977, incorporated by reference herein.)

### 30 IV. Uses of the Nondigestible Oil Compositions

The nondigestible oils, which can be processed into the flowable nondigestible oils of the present invention, can be used in frying applications such as the preparation of French fried potatoes, potato chips, corn chips, tortilla chips, chicken, fish, and battered and fried  
35 foods (e.g. shrimp tempura). Preferably, the compositions can be used as shortenings,

cooking oils, frying oils, salad oils, and popcorn oils. The compositions may also be used in cooking sprays, margarines and spreads. The individual composition components may be mixed before preparing foods or they can be added separately to the foods.

The nondigestible oils can also be used in the production of baked goods in any form, such as mixes, shelf-stable baked goods, and frozen baked goods. Possible applications include, but are not limited to, cakes, brownies, muffins, bar cookies, wafers, biscuits, pastries, pies, pie crusts, granola bars, and cookies, including sandwich cookies and chocolate chip cookies, particularly the storage-stable dual-textured cookies described in U.S. Pat. No. 4,455,333 of Hong & Brabbs. The baked goods can contain fruit, cream, or other fillings. Other baked good uses include breads and rolls, crackers, pretzels, pancakes, waffles, ice cream cones and cups, yeast-raised baked goods, pizzas and pizza crusts, and baked farinaceous snack foods, and other baked salted snacks.

The herein can also be used as a component of the fat portion of many other foods such as ice cream, frozen desserts, cheese, meats, chocolate confections, salad dressings, mayonnaise, margarine, spreads, sour cream, yogurt, coffee creamer, extruded snacks, roasted nuts and beverages, such as milk shakes.

The compositions of the present invention can be used to substitute from about 10% to 100% of the fat/oil in foods. When substituting the present compositions for fat in foods which contain fat and non-fat ingredients (e.g., starches, sugar, non-fat milk solids, etc.) the solid polyol polyesters are included to control passive oil loss of the nondigestible oil when said foods are ingested.

The compositions herein can be used in combination with other nondigestible fats, such as branched chain fatty acid triglycerides, triglycerol ethers, polycarboxylic acid esters, sucrose polyethers, neopentyl alcohol esters, silicone oils/siloxanes, and dicarboxylic acid esters. Other partial fat replacements useful in combination with the materials herein are medium chain triglycerides, triglycerides made with combinations of medium and long chain fatty acids (like the ones described in European Application 0322027 (Seiden), published June 28, 1989, incorporated herein by reference), highly esterified polyglycerol esters, acetin fats, plant sterol esters, polyoxyethylene esters, jojoba esters, mono/diglycerides of fatty acids, and mono/diglycerides of short-chain dibasic acids.

The compositions are particularly useful in combination with particular classes of food and beverage ingredients. For example, an extra calorie reduction benefit is achieved when the present flowable shortenings are used with noncaloric or reduced calorie sweeteners alone or in combination with bulking agents. Noncaloric or reduced calorie sweeteners include, but are not limited to, aspartame, saccharin, alitame, thaumatin, dihydrochalcones, acesulfame and cyclamates.

Bulking or bodying agents are useful in combination with the nondigestible oil compositions herein in many food compositions. The bulking agents can be nondigestible carbohydrates, for example, polydextrose and cellulose or cellulose derivatives, such as carboxymethylcellulose, carboxyethylcellulose, hydroxypropyl methylcellulose, hydroxypropylcellulose, methyl cellulose and microcrystalline cellulose. Other suitable bulking agents include gums (hydrocolloids), starches, dextrans, fermented whey, tofu, maltodextrins, polyols, including sugar alcohols, e.g., sorbitol and mannitol, and carbohydrates, e.g., lactose.

Similarly, food and beverage compositions can be made that combine the present nondigestible oil compositions with dietary fibers to achieve the combined benefits of each. By "dietary fiber" is meant complex carbohydrates resistant to digestion by mammalian enzymes, such as the carbohydrates found in plant cell walls and seaweed, and those produced by microbial fermentation. Examples of these complex carbohydrates are brans, celluloses, hemicelluloses, pectins, gums and mucilages, seaweed extract, and biosynthetic gums. Sources of the cellulosic fiber include vegetables, fruits, seeds, cereals, and manmade fibers (for example, by bacterial synthesis). Commercial fibers such as purified plant cellulose, or cellulose flour, can also be used. Naturally occurring fibers, such as psyllium, and fibers from whole citrus peel, citrus albedo, sugar beets, citrus pulp and vesicle solids, apples, apricots, and watermelon rinds.

These dietary fibers may be in a crude or purified form. The dietary fiber used may be of a single type (e.g., cellulose), a composite dietary fiber (e.g., citrus albedo fiber containing cellulose and pectin), or some combination of fibers (e.g., cellulose and a gum). The fibers can be processed by methods known to the art.

Of course, judgment must be exercised to make use of the present compositions and combinations thereof with other food ingredients. For example, a combination of sweetener and present flowable compositions would not be used where the specific benefits of the two are not desired. The composition and flowable composition/ingredient combinations are used where appropriate, and in appropriate amounts.

Many benefits are obtained from the use of the these nondigestible oil composition in food and beverage compositions, either when used alone or in combination with edible oils and/or other ingredients discussed above. A primary benefit is the calorie reduction achieved when nondigestible oil compositions are used as a total or partial fat replacement. This calorie reduction can be increased by using combinations of the present nondigestible oil compositions with reduced calorie sweeteners, bulking agents, or other nondigestible fats and oils. Another benefit which follows from this use is a decrease in the total amount of digestible fats in the diet. Furthermore, a significant reduction in saturated fat consumption can be achieved by substituting the present nondigestible oil compositions for saturated fats in

the diet. Foods or beverages made with the nondigestible solid fat materials instead of animal-derived triglyceride fats will also contain less cholesterol, and the ingestion of these foods can lead to reduced serum cholesterol and thus reduced risk of heart disease. Also, compositions made with these fat materials have acceptable organoleptic properties, particularly lack of waxiness.

Dietary foods can be made with the nondigestible oil compositions, to meet special dietary needs, for example, of persons who are obese, diabetic, or hypercholesterolemic. The present compositions can be a major part of a low-fat, low-calorie, low-cholesterol diet, and they can be used alone or in combination with drug therapy or other therapy. Combinations of food or beverage products made with the present nondigestible oil compositions can be used as part of a total dietary management regimen, based on one or more of these products, containing the fat materials alone or in combination with one or more of the above-mentioned ingredients, to provide one or more of the above-mentioned benefits.

This discussion of the present nondigestible oil composition uses, combinations, and benefits is not intended to be limiting or all-inclusive. It is contemplated that other similar uses and benefits can be found that will fall within the spirit and scope of this invention.

In addition to food compositions, the flowable or non-flowable nondigestible oil compositions of the present invention can be used in formulating lubricants, skin creams, pharmaceuticals, cosmetics, and the like.

The invention will be illustrated by the examples which follow the analytical methods.

#### V. Processing of Flowable Nondigestible Oil into Food and Beverage Products

The present flowable compositions are useful in the preparation of a wide variety of food and beverage products. Because of the processing steps in the present invention, the resulting flowable nondigestible oil composition, if consumed in its form directly or in foods containing the flowable nondigestible oil, may have relatively poor passive oil loss control. Consequently, it is important first to completely melt the flowable nondigestible oil to a completely molten nondigestible oil, such that the crystallized solid component, such as the solid polyol fatty acid polyester, is substantially completely melted. Preferably, the flowable nondigestible oil is melted up to a temperature of about 10°C or more above the complete melt point of the solid component. The molten nondigestible oil can then be processed into food and beverage compositions in a manner that provides sufficiently rapid cooling of the nondigestible oil in a substantially quiescent state (that is, without applying shear during the crystallization) to yield a solid polyol polyester crystalline structure that provides good passive oil loss control.

Alternatively, the flowable nondigestible oil can be applied into the food-making process directly, so long as the processing results in a substantially complete melting of the solid polyol fatty acid polyester, and subsequent rapid cooling of the molten nondigestible oil to provide the good passive oil loss control. An example of such a process is spraying of the flowable nondigestible oil onto the surface of a snack food just after frying or baking. Because the snack food is still hot, the flowable nondigestible oil will be substantially completely melted, including the solid polyol fatty acid polyester thereof, and will subsequently crystallize into a form displaying passive oil loss control as the snack food cools rapidly.

When the flowable nondigestible oil composition comprises a temperature sensitive food additive, such as a vitamin, then it is important that the time during which the nondigestible oil composition is in its re-melted state should be kept to a minimum to avoid loss of efficacy of the vitamin.

## VI. Analytical Methods

### (a). Solid Fat Content

Before determining Solid Fat Content (SFC) values, a sample of the flowable composition or mixture of nondigestible liquid/solid is heated to a temperature of 140 °F (60°C) or higher for at least 30 minutes or until the sample is completely melted. The melted sample is then tempered as follows: at 80°F (26.7°C) for 15 minutes; at 32°F (0°C) for 15 minutes; at 80°F (26.7°C) for 30 minutes; and at 32°F (0°C) for 15 minutes. After tempering, the SFC values of the sample at temperatures of 50°F (10°C), 70°F (21.1°C), 80°F (26.7°C), 92°F (33.3°C) and 98.6°F (37°C), can be determined by pulsed nuclear magnetic resonance (PNMR) after equilibration for 30 minutes at each temperature. The method for determining SFC values by PNMR is described in Madison and Hill, J. Amer. Oil Chem. Soc., Vol. 55 (1978), pp. 328-31 (herein incorporated by reference). Measurement of SFC by PNMR is also described in A.O.C.S. Official Method Cd. 16-81, Official Methods and Recommended Practices of The American Oil Chemists Society, 3rd. Ed., 1987 (herein incorporated by reference).

The slope of the SFC profile is calculated by subtracting the percent solids at 70°F from the percent solids at 98.6°F and dividing that value by 28.6.

(b). Consistency

The Consistency (K) of the nondigestible oil is measured at a temperature between 20 and 40 °C using a Rheometrics controlled stress rheometer equipped with a cone and plate measuring system. The cone diameter is 4 cm and the cone angle is 2 degrees. A sample of the nondigestible oil is carefully applied to the plate and the cone is then slowly lowered onto the sample (gap = 0.048 mm). A flow measurement is performed via the programmed application of a shear stress over time. The shear stress is increased from zero to 5,000 dynes/cm<sup>2</sup> over a 2 minutes time span. The applied stress results in deformation of the sample (i.e., strain) and the rate of strain is reported as a shear rate. These data are used to create a flow curve of log [apparent viscosity] versus log [shear rate] for the nondigestible oil sample. The flow curve is then modeled according to the following power law model:

$$\text{Apparent Viscosity} = K (\text{Shear Rate})^{n-1}$$

where the apparent viscosity is expressed in units of poise (P), shear rate is in units of 1/sec, K is the Consistency in units of P.sec<sup>(n-1)</sup>, and n is the shear index (dimensionless). The power law model is widely used to describe the flow behavior of non-newtonian materials. On the log-log plot of apparent viscosity versus shear rate, the power law model is a straight line with slope of (n-1). The shear index (n) varies from 0 to 1. The closer n is to 1, the closer the material's flow behavior is to newtonian behavior. The Consistency (K) is numerically equal to the apparent viscosity at a shear rate of 1 sec<sup>-1</sup>. The values of K and n describe the flow behavior of the nondigestible oil within specific limits of shear.

(c). Crystallization Onset Temperature

The crystallization onset temperature is that temperature at which, under the conditions of this test, turbidity is induced in the sample within 90 minutes after reaching and maintaining the crystallization onset temperature. Turbidity is caused by the first stage of crystallization.

Apparatus:

1. Jacketed, agitated, cylindrical glass flask, 4 inches in diameter, at least 250 ml volume. Heating and cooling are accomplished by circulation of a clear, uncolored fluid through the jacket. Acceptable jacket fluids are, but are not limited to, water, ethylene glycol, or silicone fluids.

2. Thermometer, calibrated in the range 25°C to 100°C.

Procedure:

1. In the flask, heat at least 250 ml of sample (but not more than 700 ml) to 85° C and hold until all solids have dissolved. Before proceeding, the solution must be clear, without any turbidity.
2. Agitate to maintain uniform temperature throughout the flask.
- 5 3. Cool at no more than 2.5°C /min to a temperature in the vicinity of the crystallization onset temperature. Note: To prevent crystallization on the vessel walls during cooling, the jacket temperature should never be any colder than 5°C below the sample temperature.
- 10 4. Hold at this temperature for 90 minutes or until the clear solution shows (by viewing horizontally through the vessel wall) the first hint of turbidity.
5. If the solution becomes turbid within 90 minutes, repeat by heating and re-dissolving the sample as in step 1. Repeat steps 2, 3, and 4, except cool to a temperature 2°C above the previous measurement.
- 15 6. Repeat until the solution does not become turbid within 90 minutes of reaching the test temperature. The crystallization onset temperature is the highest temperature at which the solution becomes turbid within 90 minutes.
- 20 7. If, on the first measurement, after 90 minutes the solution remains clear, repeat by heating and re-dissolving the sample as in step 1. Repeat steps 2, 3, and 4, except cool to a temperature 2°C below the previous measurement. The crystallization onset temperature is the highest temperature at which the solution becomes turbid within 90 minutes.

(d). Fatty Acid Composition of Polyol Polyesters

25 The fatty acid composition (FAC) of the polyol polyesters is determined by gas chromatography, using a Hewlett-Packard Model S712A gas chromatograph equipped with a flame ionization detector and a Hewlett-Packard Model 17671A automatic sampler. The chromatographic method used is described in Official Methods and Recommended Practices of the American Oil Chemists Society, 3rd Ed., 1984, Procedure 1-Ce62 (incorporated herein by reference).

30

(e). Ester Distribution of Sucrose Polyesters

35 The relative distribution of the individual octa-, hepta-, hexa- and penta- esters, as well as collectively the tetra- through mono-esters, of the sucrose polyesters can be determined using normal-phase high performance liquid chromatography (HPLC). A silica gel-packed column is used in this method to separate the polyester sample into the respective ester groupings noted above. Hexane and methyl-t-butyl ether are used as the mobile phase solvents. The ester groupings are quantitated using a mass



detector (i.e. an evaporative light-scattering detector). The detector response is measured and then normalized to 100%. The individual ester groups are expressed as a relative percentage.

5 (f). Complete Melt Point

Equipment:

Perkin-Elmer 7 Series Thermal Analysis System, Model DSC7, manufactured by Perkin-Elmer, Norwalk, Connecticut.

Procedure:

- 10 1) Sample of polyol polyester is heated to at least 10°C above the temperature at which all visible solids are melted, and mixed thoroughly.
- 2)  $10 \pm 2$  mg. of sample is weighed into sample pan.
- 3) A scan is performed from about 10°C above the temperature at which all visible solids are melted, to -60°C at 5°C per minute.
- 15 4) The temperature of the sample is maintained at -60°C for 3 minutes and scanned from -60°C to the original starting temperature at 5°C per minute (i.e. about 10°C above the temperature at which all visible solids are melted).
- 5) The complete melting point is the temperature at the intersection of the baseline (i.e., specific heat line) with the line tangent to the trailing edge of the last
- 20 (highest temperature) endothermic peak.

(g). Thickness of Solid Polyol Fatty Acid Polyester Particles (Light Microscopy)

The thickness of the solid polyol polyester particles formed in the flowable nondigestible oil compositions herein may be estimated at room temperature with a Nikon Microphot video-enhanced light microscope (VELM) using Hoffman Modulation Contrast (HMC) optics according to the following method:

- 25 1. A small portion (i.e., 1-10mg) of the nondigestible oil sample with the solid polyol fatty acid polyester particles dispersed therein is placed on a microscope slide and covered. The slide is placed under the microscope.
2. The sample is examined using a HMC 100X oil objective as the standard lens
- 30 in conjunction with a 10X eyepiece lens.
3. A microscope-mounted video camera and associated controller are used for video enhancement to facilitate differentiation between the sample and the background.
4. The thickness of the solid polyol fatty acid polyester particles is measured in
- 35 um (microns).

This method permits differentiation of particles having thicknesses just within the resolution of the VELM (approximately 0.2 - 0.5  $\mu\text{m}$ ). Particle thickness of particles having smaller dimensions can be determined by the Freeze Fracture Method described hereinafter.

5 (Note: No special sample preparation is required, other than obtaining a representative sample. The samples should be melted and cooled ambiently.)

Reference: Robert Hoffman, "The Modulation Contrast Microscope: Principles and Performances", Journal of Microscopy, Vol. 110, Pt 3, August 1977, pp. 205-222.

10 (h). Thickness of Solid Polyol Fatty Acid Polyester Particles (Freeze Fracture Transmission Electron Microscopy)

The three-dimensional topography of particles of polyol fatty acid polyesters and their size can be determined by a freeze-fracture transmission electron microscopy (ff-tem) method:

15 This freeze-fracture method is carried out as follows:

1. The outside cavity of a freezing container is filled with liquid  $\text{N}_2$  and the inner dewar of the freezing container is filled with liquid ethane (normal melting temperature of  $-172^\circ\text{C}$ ). The ethane is allowed to freeze.
2. A small amount (1-2  $\mu\text{l}$ ) of the nondigestible fat sample with the solid polyol fatty acid polyester particles dispersed therein is placed in the well of a gold-plated Balzers specimen holder. (Note: for very fluid samples, 1-2  $\mu\text{l}$  of sample is placed on a gold planchet (Balzers) and another planchet is placed on top of the first to form a sandwich.)
- 20 3. Most of the frozen ethane in the dewar is melted by inserting a metal heat sink into the dewar.
4. Immediately after melting the ethane, the specimen holder containing the nondigestible fat sample is picked up using a pair of tweezers and rapidly plunged into the liquid ethane.
5. After a few seconds, the specimen holder is removed from the ethane, quickly touched to the tip of a camel's hair brush to remove excess ethane, and immediately immersed in the liquid  $\text{N}_2$  to keep the sample cold.
- 30 6. The sample is transferred under liquid  $\text{N}_2$  to a JEOL JFD-9000C sample holder and then transferred into the chamber of a JEOL JFD-9000C freeze-fracture unit. The temperature of the unit should be about  $-175^\circ\text{C}$ . Vacuum should be at least  $8 \times 10^{-7}$  torr.
- 35 7. A knife is cooled to a temperature of about  $-165^\circ\text{C}$ .
8. The sample is fractured in the JEOL chamber using the pre-cooled knife.

9. Platinum-carbon is deposited onto the fractured sample at a 45° angle for 4.5 seconds, followed by carbon deposition at a 90° angle for 25 seconds to form a replica of the fractured sample. The high voltage is 2500V and the current is 70 mA.
- 5 10. The samples are removed from the freeze fracture unit and cleaned using 3 washes of chloroform.
11. The replica is picked up on a 300 mesh copper EM grid and examined in a transmission electron microscope.
12. Images are recorded on negative film and positive prints are made from the negatives.
- 10 13. The thickness of the polyol fatty acid polyester particles is measured in nm.

References:

- Rash, J.E. and Hudson, C.S., Freeze Fracture: Methods, Artifacts, and Interpretations, New Haven Press, New York, 1979.
- 15 Stolinski and Breathnach, Freeze Fracture Replication of Biological Tissues, Academic Press, London, 1975.
- Steinbrecht and Zierold, Cryotechniques in Biological Electron Microscopy, Springer-Verlag, Berlin, 1987.

(i) Ester Distribution of Alkoxylated Polyols using Supercritical Fluid Chromatography

- 20 The composition of the polyol ester of esterified linked alkoxylated polyols, such as esterified linked alkoxylated glycerines; and esterified epoxide-extended polyols, can be determined by supercritical fluid chromatography. A sample of polyglycerol ester is first silylated to derivatize any unreacted hydroxyl groups. The silylated sample is then injected into the supercritical fluid chromatograph (SFC). The esters are separated by
- 25 degree of esterification on a DB1 capillary column and detected by a flame ionization detector. The distribution of esters is calculated by peak area from the chromatogram.

Equipment and Conditions

SFC: Lee scientific series 6000 supercritical fluid chromatograph or equivalent;

- 30 SFC Conditions:

- A) Capillary Column  
DB1, 0.2 µ film, 50 µ ID, 10 m. J&W Scientific
- B) Temperatures  
Oven - 90 C
- 35 Detector - 400 C
- C) Pressure Program

125-375 atmospheres at 10 atmospheres per minute with a final hold time of 10 minutes.

- 5           D)    CO<sub>2</sub>  
              SFC grade, Scott Specialty Gases
- E)    Hydrogen  
              Approximately 30 mL / minute
- F)    Air  
              Approximately 300-350 mL / minute
- 10          G)    Auxiliary Gas (Nitrogen)  
              Approximately 25 mL / minute
- H)    Syringe for SFC injection  
              50 ul Hamilton
- I)    Vials
- 15          J)    Hot Plate  
              90 C
- K)    Filter  
              0.45 u Alltech Associates #2092
- 20          L)    Disposable Syringe  
              3.0 mL Fisher Scientific #14-823-39

#### Reagents

- BSTFA (bis(Trimethylsilyl)-trifluoroacetamide) Supelco, Inc. #3-3027; TMSI
- 25          (Trimethylsilylimidazole) Supelco, Inc. #3-3068; Pyridine ACS Grade MCB #PX2020-01

#### Analyzing the Sample

- The sample is melted completely and mixed well. A disposable pipet is used to weigh 80-100 mg of sample into a four dram vial. The sample weight is recorded. 1
- 30          mL of Pyridine and 1 mL of TMSI/BSTFA solution (mixed 5:1) is added to the vial. The vial is capped and heated on the hot plate at 90C for 15 minutes. The sample is allowed to cool. A 0.45-micron filter is placed on the end of a 3-cc disposable syringe. The derivatized standard is poured into the disposable syringe and filtered into a GC vial. The sample is injected into the Supercritical Fluid Chromatograph.

### Examples

Preparation of flowable nondigestible fat compositions of the present invention is illustrated by the following prophetic examples.

#### 5 Example 1. Synthesis Of A Liquid Esterified Propoxylated Glycerin.

Glycerin, 992 parts, is heated with 80 parts of 85% potassium hydroxide solution at 110°C and 10 mm in a reactor with a dry ice trap for water removal until no further water is evolved. The reactor is pressurized with nitrogen and cooled to 92°C, and 3126 parts of  
10 propylene oxide is added on a pressure demand basis maintaining a reactor pressure of 55 psi. After the propylene oxide has been added the reaction is continued for an additional 5 hours. The reactor is then cooled and purged with nitrogen. A propoxylated glycerin with a molar ratio of propylene oxide to glycerin of 5:1 is obtained.

The propoxylated glycerin and soybean methyl esters are mixed in a molar  
15 ratio of methyl esters to propoxylated glycerin of 5:1. Sodium methyle, 0.13 mole sodium methyle/mole propoxylated glycerin, is added as additional basic catalyst. The propoxylated glycerin, soybean methyl esters and catalyst are heated at 150°C for 3 hours at a pressure of 10 mm Hg in a reaction flask equipped with a distilling head for methanol. At this time the reaction mix is recatalyzed with another 0.13 mole sodium methyle/mole  
20 propoxylated glycerin and heated at 150°C for an additional 3 hours at a pressure of 10 mm Hg.

All through the purification steps, the crude reaction mix is maintained at a temperature of 80-100 C unless otherwise noted. The crude reaction mix is hydrated with 0.3% by weight water and the soap is removed by filtration. After removing the soap, the  
25 reaction mixture is washed with an 18% by weight water solution, the water solution containing 2.8% tripotassium citrate. The water phase is separated by centrifugation. The reaction mix is then washed a second time with 340% by weight water and the water phase is separated by centrifugation.

The mixture is then dried under vacuum, bleached with 1% silica gel and filtered.  
30 The excess methyl esters are removed on a Pope wiped film evaporator operating at 230 C yielding an esterified propoxylated glycerin containing both digestible and non-digestible components. The fatty acid composition and ester distribution is shown in Table A.

Example 2. Synthesis Of An Esterified, Linked Alkoxylated Polyol.

A propoxylated glycerin with a molar ratio of propylene oxide to glycerin of 4:1 is prepared by the method of Example 1. The residual catalyst is not removed. Three hundred and twenty-four parts (324) of the combined propoxylated glycerin and catalyst is mixed  
5 with of methyl behenate (708 parts giving a 2/1 mole ratio methyl behenate to propoxylated glycerin). Sodium methyleate, 0.13 mole sodium methyleate/mole propoxylated glycerin, is added as additional basic catalyst. The propoxylated glycerin, methyl behenate and catalyst are heated at 150°C at a pressure of 10 mm Hg in a reaction flask equipped with a distilling head for methanol until at least 95% conversion of the methyl behenate has occurred.  
10 Dimethyl adipate (87 grams) is added and heating continued at a pressure of 100 mm HG until at least 95% conversion of the original hydroxyl groups of initial propoxylated glycerin has occurred. The distillate comprising methanol and unreacted dimethyl adipate is periodically collected and the methanol removed on a rotovap. The unreacted dimethyl adipate is recycled to the reaction.

15 All through the purification steps, the crude reaction mix is maintained at a temperature of 80-100 C unless otherwise noted. The crude reaction mix is hydrated with 0.3% by weight water and the soap is removed by filtration. After removing the soap, the reaction mixture is washed with an 18% by weight water solution, the water solution containing 2.8% tripotassium citrate. The water phase is separated by centrifugation. The  
20 reaction mix is then washed a second time with 340% by weight water and the water phase is separated by centrifugation.

The mixture is then dried under vacuum, bleached with 1% silica gel and filtered. The excess methyl esters are removed on a Pope wiped film evaporator operating at 240 C. The fatty acid composition is shown in Table A.

25

Example 3. Flowable Liquid Polyol Polyester And Solid Polyol Polyester Mixture.

Three mixtures are made. Mixture A contains a solid sucrose polyester having fatty acid composition and ester distribution typical of those shown in Table A for the product Olean® manufactured by The Procter & Gamble Company, Cincinnati, Ohio, and a liquid  
30 esterified propoxylated glycerin from Example 1. Mixture B consists of a solid esterified linked propoxylated glycerin from Example 2 and a liquid sucrose polyester having fatty acid composition and ester distribution typical of those shown in Table A for the product Olean® manufactured by The Procter & Gamble Company, Cincinnati, Ohio. Mixture C consists of

a solid esterified linked propoxylated glycerin from Example 2 and a liquid esterified propoxylated glycerin from Example 1.

In the case of Mixture A, solid and liquid components are mixed at a proportion of 6 weight parts of the solid component to 94 weight parts of the liquid component, and agitated to a molten liquid state at a temperature of 68 °C in a temperature controlled agitated vessel. In the case of Mixtures B & C solid and liquid components are mixed at a proportion of 10 weight parts of the solid component to 90 weight parts of the liquid component, and agitated to a molten liquid state at a temperature of 68 °C in a temperature controlled agitated vessel. In each case, the molten mixture is then pumped at a flow rate of 280 pounds per hour (127.3 kg/hr.) through two serially-arranged brine-jacketed (-1.0 °C brine coolant) Cherry Burrell Votator Model 3SSHE scrapped wall heat exchangers, operating at 1690 RPM. The temperature of the mixture is lowered from 68 °C to 21 °C within a residence time of 20 seconds. Upon exiting the Cherry Burrell heat exchangers, the solid sucrose polyester portion is substantially crystallized and forms small (<10 micron) discrete and unaggregated crystal particles. The substantially crystallized composition is then passed through a heat exchanger which adjusts the temperature (as needed) to 21 °C, and into a jacketed scraped wall tank where it is held under continued shearing for two hour at 21 °C. The batch tempering tank is 12 inches in diameter and 28 inches deep, holds 100 pounds (45.5 kg) of the composition, and is equipped with an anchor-type agitator which turns at 14 rpm; there are no dead spots in the material in the vessel. In each case, the heat exchanger outlet and continued shearing hold temperature is 21 °C.

The resulting flowable nondigestible oil compositions (A, B and C) have the following physical attributes:

The liquid component has a complete melt point less than 37 °C.

The solid component has a complete melt point which is greater than 37 °C.

Substantially all of the solid component is in the form of crystallized particles.

The flowable composition has a Consistency in a temperature range of 20-40 degrees Centigrade of less than about 600 P.sec(n-1).

Table A

- 5 Fatty Acid Composition and Ester Distribution of the Solid Sucrose Polyester and the Liquid Sucrose Polyester Components of Olean®, and the Solid Esterified Linked Propoxylated Glycerin and the Liquid Esterified Propoxylated Glycerin

Fatty Acid Component	Solid Sucrose Polyester (weight %)	Liquid Sucrose Polyester (weight %)	Solid Esterified Linked Propoxylated Glycerin	Liquid Esterified Propoxylated Glycerin
C8	-	-	-	-
C10	-	-	-	-
C12	0	-	-	-
C14	0	-	-	-
C16	1.2	9.7	-	9.5
C17	0	0.1	-	0.1
C18	4.6	5.9	-	7.5
C18:1	3.7	64.5	-	58.4
C18:2	10.9	18.9	-	22.2
C18:3	0	0.2	-	1.0
C20	4.6	0.3	0.1	0.3
C22	71.7	0.2	99.8	0.4
C22:1	0.2	-	-	-
C24	2.8	-	0.1	-
Other	0.4	0.2		0.6



Ester Distribution.	%	%		
Octa	71.6	78.7		
Hepta	28.1	21.0		
Hexa	0.2	0.2		
Penta	0.1	0.2		
Tetra	*	*		
Tri			Not Characterized.	93.8%
Di				6.0%
Mono				0.2%

\* Tetra and lower esters <0.1%.

**WHAT IS CLAIMED IS:**

1. A flowable nondigestible oil composition comprising, preferably 50-99% by weight, a liquid component having a complete melt point less than 37°C; and, preferably 1-50% by weight, a solid component having a complete melt point of at least about 37°C;

wherein the solid component is in the form of crystallized particles;

wherein at least one of the liquid component and the solid component comprises a material selected from esterified linked alkoxyated polyols; esterified epoxide-extended polyols; and mixtures thereof, preferably wherein the liquid component comprises a material selected from esterified linked alkoxyated polyols; esterified epoxide-extended polyols; and mixtures thereof; and

wherein the flowable nondigestible composition has a Consistency in a temperature range of 20-40°C of less than about 600 P.sec(n-1), preferably less than about 400 P.sec(n-1), more preferably less than about 200 P.sec(n-1), most preferably less than about 100 P.sec(n-1).

2. The composition of Claim 1 wherein the solid component comprises a material selected from the group consisting of (i) a solid saturated polyol polyester, (ii) a solid diversely esterified polyol polyester, (iii) a polyol polyester polymer, and (iv) combinations thereof; most preferably wherein the solid saturated polyol polyester and the solid diversely esterified polyol polyester are in the form of co-crystallized particles.

3. The flowable nondigestible oil composition according to any of the above claims wherein the crystallized particles have a maximum dimension of from about 1 micron to about 30 microns, preferably from 2 microns to 5 microns.

4. The flowable nondigestible oil composition according to any of the above claims wherein solid saturated polyol polyester is selected from hepta-substituted saturated fatty acid polyol polyester, octa-substituted saturated fatty acid polyol polyester, and mixtures thereof, having C20-C24 saturated fatty acid radicals, preferably wherein the solid saturated polyol polyester comprises octa-behenate sucrose polyester, and wherein the solid diversely esterified polyol polyester comprises octa-saturated sucrose polyester; preferably wherein the esters are selected from behenate and a mixture of C18:1 and C18:2 unsaturate; more preferably, wherein the solid polyol fatty acid polyester has fatty acid esters comprising long chain saturated fatty acid esters and long chain unsaturated fatty acid esters in a ratio thereof of 5:3

to 7:1, preferably from 6:2 to 6.5:1.5; and wherein the solid diversely esterified polyol polyester is selected from hepta-substituted diversely esterified polyol polyester, octa-substituted diversely esterified polyol polyester, and mixtures thereof, having fatty acid radicals comprising a) long chain saturated fatty acid radicals, and b) dissimilar fatty acid radicals which are dissimilar from the long chain saturated fatty acid radicals and are selected from the group consisting of i) long chain unsaturated fatty acid radicals, ii) short chain saturated fatty acid radicals, and iii) mixtures thereof; most preferably, wherein the solid saturated polyol polyester is a sucrose polyester comprising at least 5% by weight sucrose octabehenate, and preferably the solid sucrose polyester has a complete melt point of at least about 60 °C.

5. A process for making a flowable nondigestible oil composition comprising a liquid component having a complete melt point less than 37°C, and a solid component having a complete melt point of at least about 37°C, the process comprising the steps of:

a) providing a mixture comprising the liquid component and the solid component, wherein at least one of the liquid component and the solid component comprises a material selected from esterified linked alkoxyated polyols; esterified epoxide-extended polyols; and mixtures thereof ;

- b) melting the nondigestible oil comprising the solid component and the liquid component,
- c) crystallizing at least a substantial portion of the solid component, preferably wherein said crystallization is accompanied by
  - i) reducing the temperature of the melted nondigestible oil to a crystallization temperature less than the onset crystallization temperature of the solid component;
  - ii) holding the nondigestible oil at the crystallization temperature for a time sufficient to crystallize at least a substantial portion of the solid component; and more preferably wherein the crystallizing step further comprises continued holding the crystallized composition at a crystallization temperature whereby the crystallization of the solid component is substantially complete; and
- d) shearing the nondigestible oil composition during the step of crystallizing, thereby forming the solid component into crystallized particles, preferably wherein the shearing further comprises continued shearing of the composition during the continued holding step;

wherein the flowable nondigestible oil has a Consistency in a temperature range of 20 ° to 40°C of less than about 600 P.sec(n-1), preferably wherein the step of crystallizing and step of shearing are both conducted in a scraped wall heat exchanger or equivalent.

6. The process according to Claim 5 wherein the crystallization temperature is about 5° C or more below the onset crystallization temperatures of the solid component.
7. The process according to any of Claims 5 or 6 wherein the flowable nondigestible oil composition has a Consistency in a temperature range of 20°-40°C of less than 400 P.sec(n-1), preferably less than 200 P.sec(n-1); more preferably less than 100 P.sec(n-1).
8. The process according to any of Claims 5-7 wherein the solid component has a complete melt point of at least 60 °C.
9. The process according to any of Claims 5-8 wherein in at least 80%, preferably at least 95%, of the solid component is crystallized, preferably wherein the solid component is crystallized at a crystallizing temperature of at least about 10 °C below the onset crystallization temperature of the solid component, more preferably wherein crystallizing comprises cooling the composition from the molten temperature to the crystallization temperature at a cooling rate of about 100 - 300 °C/min., most preferably wherein crystallizing is completed within about 30 seconds.
10. The process according to any of Claims 5-9 wherein the step of shearing comprises shearing the crystallizing composition at a shear rate of about 400 sec<sup>-1</sup> to about 8000 sec<sup>-1</sup>, preferably wherein a diluting amount of the liquid component is added to the crystallized composition in a ratio of from about 0.5:1 to about 0.1:1; most preferably further comprising the step of adding a stabilizing amount of a diluent liquid after the step of crystallizing the solid polyol fatty acid polyester.
11. The process according to any of Claims 5-10 further comprising the step of tempering the flowable nondigestible oil composition by reducing the temperature of the composition to a tempering temperature which is below an intended storage temperature, and preferably shearing the tempered composition.

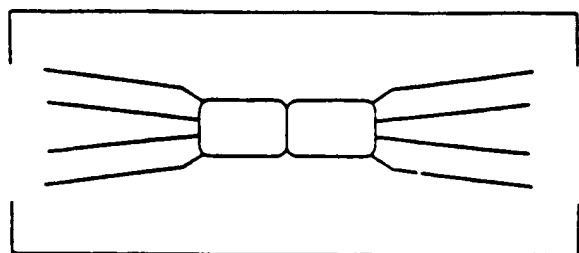


Fig. 1A

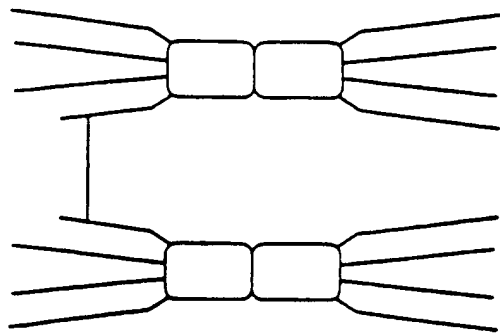


Fig. 1B

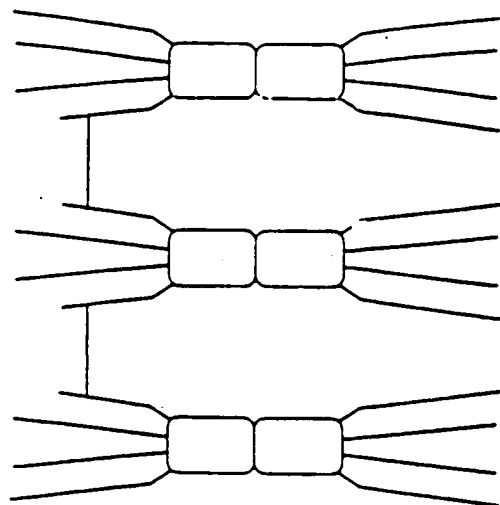


Fig. 1C

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